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Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber. User's Guide

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MEASUREMENT OF GASEOUS EMISSION RATES FROM LAND SURFACES USING AN EMISSION ISOLATION FLUX CHAMBER

USER'S GUIDE

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A promising method for monitoring ground emissions involves the use of an emission isolation flux chamber. The method is simple, easily available, and inexpensive. Applications would include RCRA and CERCLA facilities. To date, a uniform method operations does not exist. For this reason, an operations guide has been developed. This guide presents literature surveys, operation protocols, a case study, and references for further reading. The use of this protocol will aid in unifying flux chamber measurements and increase data comparability.

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SECTION 1

INTRODUCTION

Volatilization of organic compounds from contaminated soil or groundwater into the air represents a major potential source of exposure which has not been assessed. In order to assess this exposure potential, a method is needed to directly measure gas emission rates from contaminated soils and/or groundwater. Additionally, it is recognized that an understanding of the volatilization, transport, and emission processes could lead to a predictive tool for exposure assessment. The information provided by direct measurement and/or predictive modeling will allow state and local regulatory agencies to develop programs to assess and define the need to control gas emissions from area sources contaminated by organic compounds.

The purpose of this User's Guide is to present an approach and protocol, namely the emission isolation flux chamber (or flux chamber) technique, for measuring emission rates of volatile organic compounds from contaminated soils and/or groundwater. Presented is the theory of operation, specifications, sensitivities, method of operation, and data reduction procedures for this technique. It is assumed that the individuals who will use the protocol are, in general, familiar with sample collection and analysis of volatile organic compounds. Also included in this document is a case study that demonstrates the measurement and data reduction processes around a spill site.

The flux chamber technique is applicable to the measurement of emission rates from Resource Conservation and Recovery Act (RCRA) facilities (hazardous waste landtreatment, and landfill facilities), and from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) area sources contaminated by losses of volatile organic compounds from spills, from leaking underground storage tanks, from pipelines, and/or from surface impoundments.

This protocol does not present the vast amount of work that was required to develop this document. Rather, the protocol is a result of literature reviews selecting a measurement technique and field applications demonstrating the technique and developing a data base and validation studies identifying the method of flux chamber operation. References to the other area sources where this technique was applied, the work performed to validate the technique, and the investigations of variables which control the emission process are also given for those individuals desiring further information.

SECTION 2

BACKGROUND

The following subsections discuss the process by which volatile organic compounds are emitted from contaminated land surfaces, the basis upon which the flux chamber technique was selected as an approach for measuring such emission rates, and the principle of the technique.

2.1 Emission Processes

The rate of volatile organic compound (VOC) emissions from contaminated soils is generally believed to be controlled by the diffusion rate of the chemical compound through the air-filled pore spaces of the soil.(1,2,3) The exception occurs when the contaminated material lies on or very near the soil surface. Such is the case when spills occur or immediately after waste is surface-applied to a landtreatment site. In these cases, the emission process will be controlled by the rate of evaporation.

Evaporation is a surface phenomenon, and the parameters that affect the evaporation process are the properties of the waste itself as well as those that have an effect on the air-surface interface (i.e. wind, surface roughness). The important parameters include the volatility or vapor pressure of the waste, ambient meteorological conditions (solar insolation, air and waste temperature, surface wind speed, relative humidity), surface coarseness, and the bulk concentration of the volatile components in the air (although this is usually very low and generally assumed to be negligible).

There are two major types of soil emission processes. Each are treatment dependent. One type occurs in landtreatment facilities and the other at underground facilities such as landfills. In landtreatment applications, the emission rate is generally highly time-dependent. When a fixed amount of waste is applied to the soil surface, it penetrates the soil to a certain depth. The vaporization rate is maximum immediately after waste application, as the material nearest the surface is vaporized and diffuses through a very thin layer of soil. As the waste near the surface is depleted of its VOC content, the volatile material deeper in the soil must diffuse through an increasingly thick soil layer. The soil presents a resistance to VOC diffusion in direct proportion to the VOC depth. Thus, the rate of emissions from the surface decreases with time.

It is common practice in landtreatment to periodically till the soil to provide oxygen for bacterial activity. The tilling effectively mixes the remaining waste in a homogeneous layer near the soil surface. The emission rate is at a maximum immediately following each tilling episode since

volatile waste is again present very near the surface, and resistance to diffusion is at a minimum.

Although also diffusion controlled, the emission process from underground sources such as landfilled waste or material present as a "lens" on the water table has significantly different characteristics than that from surface or near-surface sources. The depth of the emission source is usually quite substantial. Therefore, the emission rate is initially lower due to the resistance to diffusion produced by the coloumn of soil. The initial emission rate is zero, since it takes some time for the volatile material to diffuse through the soil layer. The adsorptive sites on the soil particles must also be initially saturated. Once the emission rate has equilibrated, the rate is relatively constant with time until the underground source is exhausted.

The diffusion process itself through the soil is the same for both types of sources, landtreatment (surface) and landfill (underground). Consequently, many of the parameters important to the emission processes are the same, including diffusivity of the VOC in air, soil properties (particle size distribution, soil type, moisture content, particle density, porosity), soil/waste temperature, and volatility of the VOC in the waste. Additional parameters important to the near surface emission processes are the amount of material present in the contaminated soil layer, the initial depth of the contamination, the elapsed time from application (or filling) and, possibly, ambient conditions such as surface wind speed and relative humidity. The depth of the soil layer above the waste is a very important parameter in the emission process from subsurface sources. Additionally, the adsorptive properties of the soil may also have a significant effect on the emission rate from this latter source type.

An understanding of the emission processes and the important parameters is necessary in the measurement of emission rates from soil surfaces and in the proper interpretation of the test results. As an example, the emission rate from a source is affected by rain since the porosity and, hence, the diffusion rate are reduced with increasing moisture content of the soil. Thus, emission rates immediately after a rainfall will be lower than those from drier soils and may take substantial periods of time to return to the emission rate prior to the rain.(4) Emission rates may vary with the time of day and season, as a result of changes in ambient and soil/waste temperatures.(4) Emission rates from soil areas containing fissures can be higher and much less homogeneous than those from unfractured areas. Thus, considerable care must be taken in planning and implementing a measurement program to determine representative emission rates from such soil surfaces.

2.2 Measurement Techniques

Based on a literature review (5), the techniques for determining gas emissions rates from land surfaces contaminated with organic compounds can be divided into three approaches: indirect measurements, direct measurements, and laboratory simulations. Indirect techniques typically require measurements of ambient air concentrations at or near the site. These

measurements are related to the surface area of the area source and local meteorological conditions using a dispersion model to determine an emission rate. The second approach is to directly measure emission rates using for example the flux chamber. The third approach is to create an emission source in the laboratory and model the emissions by various techniques for application to field sites. These three approaches were compared for precision, accuracy, and sensitivity. Other considerations included applicability, complexity, manpower requirements, and costs.

The most promising technique for measuring gas emission rates from land surfaces was determined to be the emission isolation flux chamber technique. The advantages are:

- lowest (most sensitive) detection limit of the methods examined;
- easily obtained accuracy and precision data;
- simple and economical equipment relative to other techniques;
- minimal manpower and time requirements;
- rapid and simple data reduction; and
- applicable to a wide variety of surfaces.

2.3 Flux Chamber Operation

The flux chamber technique has been used by researchers to measure emission fluxes of sulfur, nitrogen, and volatile organic species (6,7,8,9,10). The approach uses a flux chamber (enclosure device) to sample gaseous emissions from a defined surface area. Clean dry sweep air is added to the chamber at a fixed, controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is calculated as:

$$E_I = Y_I Q/A \qquad (2\text{-}1)$$

where: E_I = emission rate of component I (mass/area-time),
Y_I = concentration of component I in the air flowing from the chamber (mass/volume),
Q = flow rate of air into the chamber (volume/time),
A = surface area enclosed by the chamber (area).

All parameters in Equation 2-1 are measured directly.

Most of the emission rate assessments are of area sources much larger than the enclosed surface area of the flux chamber (0.130 m^2). In these

cases, an overall emission rate for the area source is calculated from multiple measurements based on random sampling and statistical analysis.

SECTION 3

MEASUREMENT OF GASEOUS EMISSION RATES FROM LAND SURFACES USING AN EMISSION ISOLATION FLUX CHAMBER - PROPOSED METHOD

3.1 Applicability and Principle

3.1.1 Applicability

The flux chamber technique is applicable to the measurement of emission rates from Resource Conservation and Recovery Act (RCRA) facilities such as hazardous waste landtreatment and landfill facilities. This technique is also applicable for emission rate measurements from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) waste sites such as areas contaminated by losses of volatile organic compounds from spills, from leaking underground storage tanks, from pipelines, and/or from surface impoundments.

3.1.2 Principle

Gaseous emissions are collected from an isolated surface area with an enclosure device called an emission isolation flux chamber (or flux chamber). The gaseous emissions are swept through an exit port where the concentration is monitored and/or sampled. The concentration is monitored and/or sampled either continuously (i.e., "real-time") or discretely. Real-time measurements are typically made with portable total hydrocarbon analyzers and are useful for relative measurements (i.e., the determination of flux chamber steady-state operation, zoning). Discrete samples are taken when absolute measurements are necessary (i.e., steady-state concentrations, emission rate levels). The emission rate is calculated based upon the surface area isolated, the sweep air flow rate, and the gaseous concentration measured. An estimated average emission rate for the area source is calculated based upon statistical sampling of a defined total area.

3.2 Precision, Accuracy, Sensitivity, and Range

3.2.1 Precision

Single chamber precision (i.e., repeatability) of the method is approximately 5 percent at measured emission rates of 3,200 ug/min·m^2. Variability between different flux chambers (i.e., reproducibility) is approximately 9.5 percent within a measured emission rate range of 39,000 to 65,000 ug/min·m^2.(4)

The reproducibility results were determined from a bench-scale study. The tests were designed to eliminate temporal variations from the flux chamber reproducibility. However, using the same bench-scale facility, a test design was not possible for measuring flux chamber repeatability without bias from temporal variations. As a result, the repeatability tests were performed in the laboratory. The differences therefore between the stated emission rates for repeatability and reproducibility reflect the differences in laboratory simulated emission rates and those meausred from the bench-scale facility.

3.2.2 Accuracy

Flux chamber recovery (Section 3.6.1.4.2) results show a recovery range of 77 percent to 124 percent. Table 3-1 lists measured recoveries for a number of compounds tested. The average recovery for the 40 compounds tested is 103 percent.

Flux chamber emission rate measurements made on the soil cells range from 50 percent to 100 percent of the predicted emission rates. That is, the measured emission rates can be expected to be within a factor of one-half of the "true" emission rates.(4) The flux chamber accuracy based upon both the recovery tests and predictive modeling ranges from 50 percent to 124 percent.

3.2.3 Sensitivity

The sensitivity of this method depends on the detection limit of the analytical technique used. When discrete samples are collected using gas canisters and analyzed by gas chromatographic methods, the estimated emission rate sensitivity is 1.2 ug/min·m^2 for an analytical detection limit of 10 ppbv benzene. When emission rates are measured in a continuous (real-time) method, the estimated sensitivity is 124 ug/min·m^2 for an analytical detection limit of 1 ppmv benzene.

3.2.4 Range

The range of this method depends upon the analytical technique used. High level emission rates are analyzed by introducing proportional amounts of gas sample to the analyzer. Using this technique, high level emission rates of 120,000 ug/min·m^2 have been measured.(4) Low levels are limited by the sensitivity of the analytical technique. Gas chromatographic techniques have been used to measure low level emission rates of 1.2 ug/min·m^2 for measured concentrations of 10 ppbv benzene.

3.3 Interferences

3.3.1 Flux Chamber Method

Impurities in the sweep air and/or organic compounds outgassing from the transfer lines and acrylic chamber top may cause background contamination. The emission isolation flux chamber must be demonstrated to be free

TABLE 3-1
COMPOUNDS TESTED IN THE EMISSION ISOLATION FLUX CHAMBER
AND THE MEASURED PERCENT RECOVERY

Compound	Percent Recovery*	Compound	Percent Recovery*
Total C_2	100	3-methylhexane	106
Total C_3	108	2,2,4-trimethylpentane	106
Isobutane	109	n-heptane	103
1-butene	108	Methylcyclohexane	103
n-butane	106	Toluene	103
t-2-butene	107	Ethyl benzene	94.7
c-2-butene	109	mtp-xylene	88.5
Isopentane	112	o-xylene	97.3
1-pentene	105	n-nonane	99.4
2-methyl-1-butene	124	n-propylbenzene	95.5
n-pentane	107	p-ethyltoluene	92.5
n-pentene	103	1,3,5-trimethylbenzene	93.5
c-2-pentene	105	1,2,4-trimethylbenzene	88.7
Cyclopentene	105	2-methyl-2-butene	103
n-hexane	95.1	Methyl mercaptan	107
Isohexane	107	Ethyl mercaptan	107
3-methylpentane	106	Butyl mercaptan	101
Methylcyclopentane	105	Tetrahydrothiophene	115
Benzene	106	Trichloroethylene	77.1
1,2-Dimethylpentane	105	Ethylene dichloride	103

*Section 3.8.2

from significant (<10 percent of expected measured concentrations) levels of such contamination under the measurement operating conditions by running method blanks. Background levels above this limit will significantly bias the flux chamber measurements. Typical values measured with a real-time analyzer (OVA) range from 0 to 2 ppmv exit gas concentration.

Cross-contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of cross-contamination, the chamber should be purged between samples with ultra high purity air and followed with running a method blank until typical values are achieved.

The use of a transparent chamber may result in gas and surface warming due to greenhouse effects. The degree of gas and surface warming are dependent upon the outside air temprature. For outside air temperatures of 28°C, a temperature gradient between the inside flux chamber air and outside air increases from 9°C at 5τ (30 minutes) to 30°C 2.5 hours later. Such heating is minimized by the use of short sampling times.

As a result of the greenhouse effect, condensation may occur when monitoring moist surfaces. Condensation should be recorded when observed and dried from chamber surfaces and lines between sample runs. Condensation could reduce exit gas concentrations of water soluble compounds.

The emission rate process from soils enclosed by the flux chamber could be suppressed as the internal VOC vapor phase concentration increases. Emission rate suppression is avoided by increasing the sweep air flow rate. Suppression is not a significant factor until flux chamber entrapped vapor concentrations are greater than 10 percent of the equilibrium vapor phase concentration. The equilibrium vapor phase concentration is determined from the headspace concentration measurements of a soil sample. This concern applies only when sampling highly concentrated and volatile waste.

3.3.2 Emission Process

Ground moisture resulting from either rain, heavy dew, etc. has a definite effect upon the emission rate from land surfaces. Ground moisture accumulation from trace amounts of rain ($\leq$0.01 inches) have little or no effect, whereas ground moisture resulting from a rainfall of 0.30 inches of water has been observed to decrease emission rates by 90 percent.(4) At this level of precipitation, seven days of hot, sunny weather were required before the gas emission rates returned to values equal to that before the rain. As such, emission rate measurements made on soils recently experiencing an elevated ground moisture content would be biased. Emission rate measurements will be below those made at normal soil moisture levels.

3.4 Apparatus and Materials

3.4.1 Flux Chamber and Supporting Equipment

A diagram of the flux chamber and supporting equipment is shown in Figure 3-1. The flux chamber materials and specifications are listed in

FIGURE 3-1
A CUTAWAY DIAGRAM OF THE EMISSION ISOLATION FLUX CHAMBER AND SUPPORT EQUIPMENT

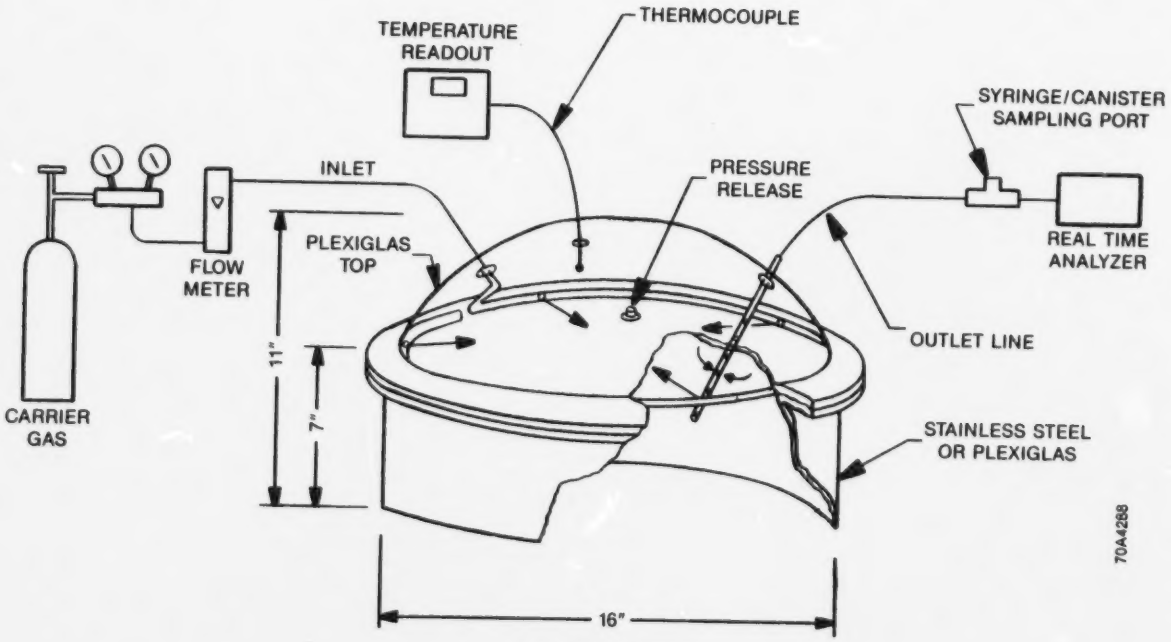


Table 3-2. A construction diagram of the flux chamber is shown in Figure 3-2.

The sweep air carrier gas should be dry, organic free air equal to or better than commercial ultra high purity grade (<0.1 ppmv THC). A gas flow meter with no internal rubber parts and adjustable within the range of 1-10 L/min should be used to control gas flow. Temperature measurements should be made with an accuracy of ±1.0°C. A fine-wire thermocouple with electronic readout is recommended. Caution should be taken to avoid any contact of a thermocouple with metal. This would give inaccurate air temperature readings. A pressure release port is required to avoid pressure build-up inside the flux chamber during operation. This port should never be blocked. For system blanks, a clean Teflon™ sheet should be used to provide a clean surface for the flux chamber.

3.4.2 Discrete Sample Collection

Discrete grab samples should be collected with air-tight, inert containers. For on-site analysis, 100 ml precision lock, glass syringes are recommended. Glass plungers are recommended over Teflon™ tip plungers. If Teflon™ tip plungers are used, then special controls must be followed to avoid cross-contamination (Section 3.7.1.1). For samples to be transported or to be stored for periods longer than 1 hour, 2L stainless steel gas canisters are recommended.

3.4.3 Analysis

3.4.3.1 Real Time

Analyzer

For real-time, continuous monitoring of the exit gas concentration, analyzers with precision of ±10 percent of the measured value and a detection limit of 1 ppmv are recommended.

Calibration Gases

The portable, real-time analyzers will require the following levels of calibration gases:

- High-Level Gas: Concentration within 50 percent to 90 percent of the span value (maximum expected concentration or upper limit of instrument linear range).
- Low-Level Gas: Concentration less than or equal to 0.01 percent of the span value.
- Zero Grade Gas: Ultra high purity (UHP) air (<0.1 ppmv THC).

The calibration gas for these analyers can be the same as that used for the on-site discrete analyzer (Section 3.4.3.2.2).

TABLE 3-2
FLUX CHAMBER MATERIALS SPECIFICATIONS

Item	Description	Specification
Carrier Gas Lines:		
Inlet/Outlet	Teflon™ (clear)	1/4" OD, 5' to 8' long, thin walled, 1/4" stainless steel fittings
Sweep Air Wrap Perforation[a]	Stainless Steel four equidistant holes jetting direction	1/4" OD, 54" long, perforated hole No. 1 (nearest input), 5/64" ID, holes No. 2-4, 3/32" ID, axially, horizontally
Fittings[b]	Stainless steel	1/4" bulkheads with teflon washers for chamber penetration
	Stainless steel	1/4" cap to seal wrap line end
Thermocouples		
Air (1)	Fine wire K type	36" long, bead tip, teflon coated (extensions optional), penetrate flux chamber 3", support with 1/4" bulkhead with septa
Flux Chamber:		
Base	Stainless steel column	16" ID x 7" tall, welded to a support ring flange
Support ring flange	Stainless steel	16" ID x 20" OD x 1/4" thick
Dome	Acrylic	Spherical, 4" displacement at center, 16" ID at seal, 2" lip for seal, 1/4" thick, molded
	four holes	Equidistant, 4" from aluminum gasket
	Inlet/outlet	1/2" ID with 1/4" stainless steel bulkhead
	Air temperature	1/2" ID with 1/4" stainless steel bulkhead
	Pressure release	13/16" ID with 3/4" stainless steel bulkhead
Seal		
Dome to Base	Top gasket	Aluminum 16" ID, 20" OD, 1/4" thick
	Dome lip	Below aluminum gasket is the acrylic lip of dome

(Continued)

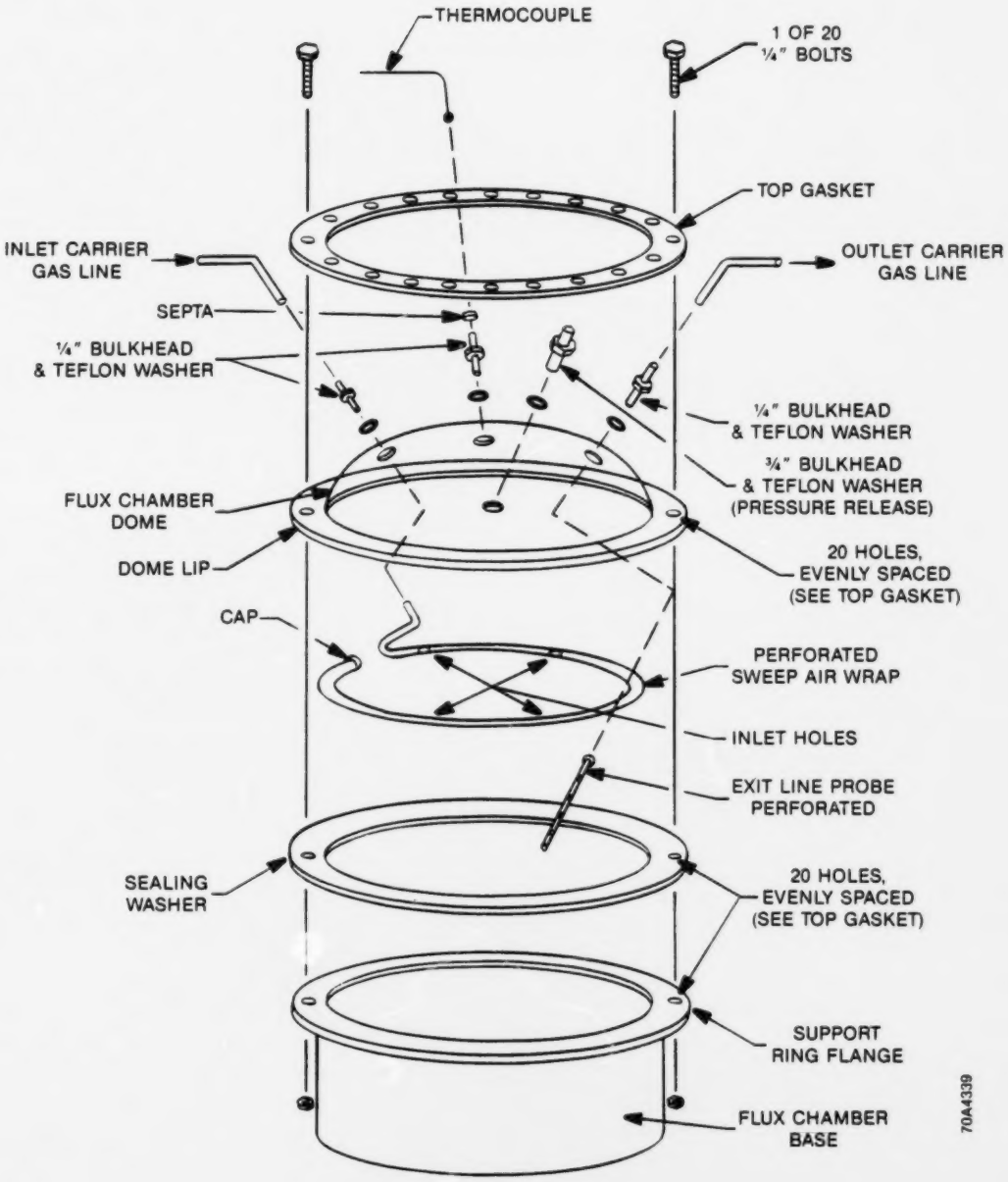
TABLE 3-2
(Continued)

Item	Description	Specification
	Sealing washer	Teflon, 16" ID, 20" OD, 1/32" thick
	Bottom gasket	Stainless steel support ring
	Fasteners	20, 1/4" bolts equidistant around lip
Volume	With 1" soil penetration	0.03 m^3 (30L)
Surface Area	Enclosed by chamber	0.130 m^2
Exit Line Probe	Teflon™	1/4" OD, 6" long, stainless steel fitting, perforated
Perforation	2 rows of holes	3/32" ID, 5 holes per row, 1" separation, rows are positioned orthogonally

[a]Avoid placement of exit line probe in jetting path of sweep air inlet holes

[b]All fittings are manufactured by Swagelok® or equivalent manufacturer (bulkheads use Teflon™ washers for sealing)

FIGURE 3-2
EXPLODED VIEW OF THE FLUX CHAMBER



Quality Control (QC) Gas

The portable, real-time analyzer will require a quality control (QC) gas concentrated to fall within the span range. The QC gas for this analyzer can be the same as that used for the on-site discrete analyzer.

3.4.3.2 Discrete

Analyzer

The analyzer should be sensitive with low detection limits. For on-site analysis of grab samples, instrumentation having precision of ±5 percent of the measured value with a detection limit of 1 ppm is recommended. Analyzers with injection loops are recommended to reproduce the sample volumes injected. For off-site analysis, instrumentation with precision of ±30 percent at detection limits of 1 ppbv are recommended.

Calibration Gases

The concentrations and composition of the calibration gases to be used will vary depending on the species of interest. Preferably, the following gas concentrations should be used for each species of interest:

- High-Level Gas: 90 percent of the span value.
- Mid-Level Gas: Average expected concentration.
- Low-Level Gas: 0.01 percent of the span value.
- Zero Grade Gas: Ultra high purity (UHP) air, (<0.1 ppmv THC).

Alternatively, a high-level gas may be used with a dilution system to generate the lower level gas concentrations. A dilution system is recommended that meets or exceeds that described in Section 6.2.1.1 of Method 18 of 40 CFR Part 60. If multicomponent species are analyzed, then on-site calibration gases should be benzene or hexane. To identify and quantitate multicomponent responses when a single component (benzene or hexane) is used for calibration, a library of normalized responses relative to the single component calibration gas must be employed. This does not guarantee all species of the multicomponent will be identified. If specific identification and quantitation are not required, then quantitation and identification should be made relative to the calibration gas.

QC Gas

The discrete analyzer will require a QC gas that has a concentration within the span range.

3.5 Procedure

3.5.1 Flux Chamber Operation

The flux chamber is operated identically for real-time and discrete sampling.

3.5.1.1 Preparation

All exposed chamber surfaces should be cleaned with water and wiped dry prior to use. Assemble the sampling apparatus and check for malfunctions and leaks.

3.5.1.2 Operation

Place the flux chamber over the surface area to be sampled and work it into the surface to a depth of 2-3 cm. Initiate the sweep air and set the flow rate at 5 L/min. Record data at time intervals defined by residence times or τ (tau), where 1τ = flux chamber volume (30L)/sweep air flow rate (5L/min). One τ then has the value of 6 minutes under normal operating conditions. At $\tau = 0$ (flux chamber placement), record the following: time, sweep air rate, chamber inside air temperature, ambient air temperature, and exit gas concentration (real-time analyzer). The data should be recorded on the data sheet shown in Figure 3-3. At each residence time (τ, 6 minutes), the sweep air rate shall be checked (and corrected to 5 L/min if necessary), and the gas concentration shall be recorded (real-time analyzer). After 4 residence times (24 minutes), initiate sample collection. At this time, record the following data: time, sweep air rate, air temperatures inside and outside, exit gas concentration, and sample number(s). If sulfonated organic compounds are of specific interest, then measurements should be taken after 10 residence times (1 hour).

3.5.2 Sample Collection

3.5.2.1 Real Time

When real-time monitoring is required, the sample is collected by the real-time analyzer directly from the exit gas line.

3.5.2.2 Discrete Sample Collection

Sample collection should not exceed a flow rate of 2 L/min.

Gas Syringes

Sample collection with syringes should be performed after purging the syringe three times with the sample gas. This should be performed without removing the syringe from the sampling line manifold. To ensure fresh sample at each purge, a sampling manifold should be positioned prior to a real-time analyzer (Figure 3-1). The analyzer will then draw the sample past the manifold for sampling.

FIGURE 3-3
FLUX CHAMBER GAS EMISSION MEASUREMENTS FIELD DATA SHEET

FLUX CHAMBER EMISSIONS MEASUREMENT DATA

Date_____ Sampler(s)_____

Location _____ Zone/Grid Point _____

Surface Description _____

Concurrent Activity _____

Time	Sweep Air Rate, Q (L/Min)	Residence No. (Q/V)	Gas Conc. (ppmv)	Air Temperature Chamber (C)	Air Temperature Ambient (C)	Sample Type/No.	Comments:	
		0						
		1						
		2						
		3						
		4						
		5						

Comments:_____

_____

_____

7-86-24843

Gas Canister

Sample collection with evacuated gas canisters should be performed with the real-time analyzer replaced by the gas canister (Figure 3-4).

To collect canister samples, remove the real-time analyzer from the exit line sampling manifold. Securely fasten the canister sampling manifold to the exit line manifold. Open the flow control valve (V_1, Figure 3-4) slightly. If this valve is opened too much, the large pressure drop at the exit line inside the flux chamber could draw direct air jetting from the sweep air inlet manifold. This would reduce the measured emission rate. A large pressure drop inside the flux chamber could also draw ambient air in through the pressure release port. These concerns are important only when the exit line sampling rate approaches that of the entrance sweep air rate (5 L/min). If a 2L gas canister is used, then control the flow to fill the canister in 1 to 2 minutes. The use of a capillary flow controller between the exit line and canister could be used to control gas flow.

After sample collection, seal the sample valve (V_1) prior to removal from the sampling line. This prevents contamination. At this time, the sample is labeled and recorded. Record the final pressure of the canister.

3.5.3 Sample Analysis

3.5.3.1 Real Time

Real-time analysis is a continuous process with the real-time analyzer connected to the exit line. These data are an initial indication of the exit line concentration.

3.5.3.2 Discrete

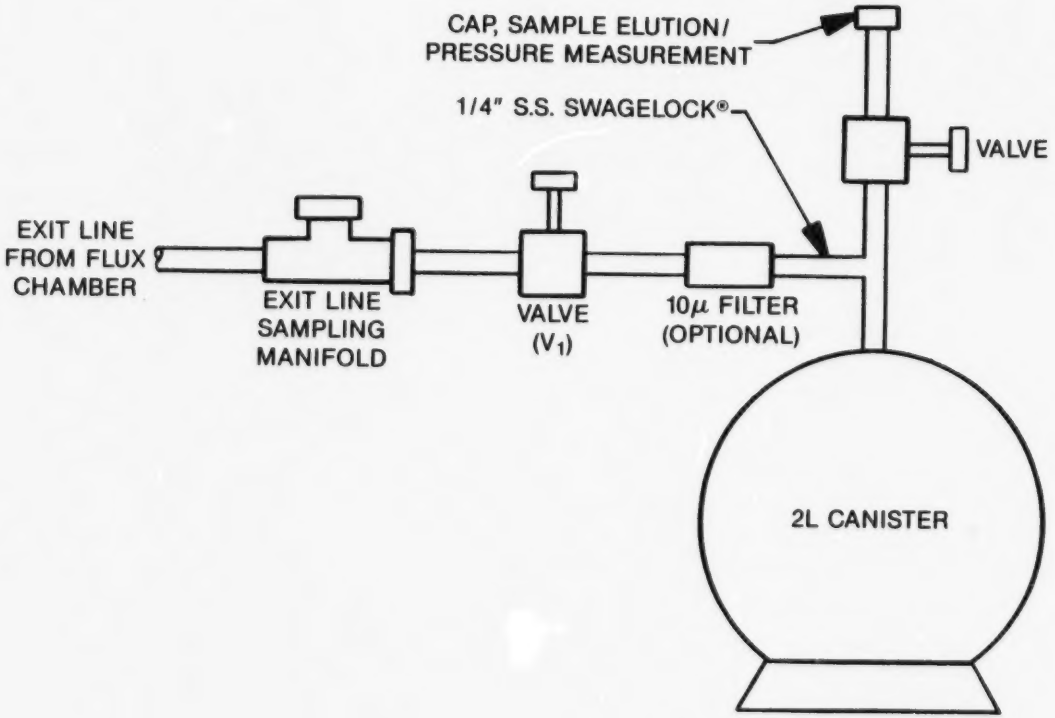
Gas Syringes

Gas syringe samples collected should be treated promptly and consistently. Temperature differentials between the flux chamber air and the analytical laboratory air can cause changes in sample volume. It is recommended that the analytical air temperature be constant, recorded twice daily and within 10°F of the ambient outside air temperature. The samples should be analyzed either immediately upon arrival into the analytical area or allowed to thermally equilibrate (1-5 min depending on syringe size). Since immediate analysis is not always possible, the later technique is recommended.

Gas Canisters

Prior to sample preparation for analysis, the canister pressure should be measured. The canisters are then pressurized to 18 psi with ultra high purity nitrogen. Measure the final pressure. A known volume of diluted gas canister sample is taken from the canister by releasing sample into an evacuated volumetric stainless steel canister (3.55L). From this volumetric

FIGURE 3-4
STAINLESS STEEL GAS CANISTER AND SAMPLING MANIFOLD
(NOT TO SCALE)



gas canister, the sample is then introduced into the gas chromatograph through cryogenic traps. The dilution factor is calculated by Equation 3-2 (Section 3.8.3).

3.5.4 Sampling Strategy

The following sampling strategy provides an accurate and precise estimate of the emission rate for a total area source through random sampling in which any location within the area source has a theoretically equal chance of being sampled. The sampling strategy described below provides an estimated average emission rate within 20 percent of the true mean with 95 percent confidence.

3.5.4.1 Zones

Based on area source records and/or preliminary survey data, subdivide the total area source into zones if nonrandom chemical distribution is exhibited or anticipated. The zones should be arranged to maximize the between-zone variability and minimize the within-zone variability.

3.5.4.2 Grids

Divide each zone by an imaginary grid with unit areas that depend on zone area size (Z) as follows:

If $Z \leq 500$ m^2, then divide the zone area into units with areas equal to 5 percent of the total zone area (i.e., 20 units total).

If 500 $m^2 < Z \leq 4{,}000$ m^2, then divide the zone area into units of area 25 m^2.

If 4000 $m^2 < Z \leq 32000$ m^2, then divide the zone area into 160 units.

If $Z > 32000$ m^2, then divide the zone area into units with area equal to 200 m^2.

Assign a series of consecutive numbers to the units in each zone.

3.5.4.3 Sample Number

Using Equation 3-3 (Section 3.8.4), calculate the number of units (grid points) to be sampled for the Kth zone (n_K).

3.5.4.4 Sample Locations

Using the random numbers table (Appendix A), identify n_K grid points (units) that will be sampled in zone K. A grid point shall be selected for measurement only once. (This is not to be confused with duplicate sampling, Section 3.7.2.2.)

3.5.4.5 Emission Rate Calculations

After sample collection, use Equations 3-4, 3-5, 3-6, 3-7, and 3-8 to calculate the measured emission rate (E_{cKI}) for each grid point (I) in each zone (K). Research has shown an emission rate dependency upon the air temperature inside the flux chamber.(4) Through a statistical analysis of both laboratory and field data, a correction factor for temperature variations has been developed. The correction factor compensates a measured emission rate for chamber air temperature variations from the nominal chamber air temperature.

The nominal chamber air temperature can be defined in two ways depending on the purpose of emission rate measurements. If emission rate measurements are for an estimate of an area source, then the nominal chamber air temperature should be the mean chamber air temperature of all the measurements made at that area source. If emission rate measurements are compared between area sources, then the nominal chamber air temperature should be 25°C (298K).

3.5.4.6 Preliminary Estimates

With Equations 3-9, 3-10, and 3-11, calculate the zone mean emission rate ($\bar{E}_K$), variance (S_K^2), and coefficient of variation (CV_K), respectively. For these calculations, use the first emission rate measurement of a duplicate set.

3.5.4.7 Further Sampling

Use Table 3-3 and CV_K to determine the total number of samples (N_K) required from a given zone to estimate with 95 percent confidence an emission rate within 20 percent of the mean. If $N_K > n_K$, then $N_K - n_K$ additional samples must be collected from zone K. Locate these additional samples using a random numbers table. Do not duplicate previously sampled locations.

If $N_K >> n_K$, it may be most effective to rezone using the preliminary measured emission rates as a guide. If new zones are established, then these new zones will need to be gridded accordingly (Section 3.5.4.2).

3.5.4.8 Final Estimates

Collect any additional samples and recalculate the emission estimates for the sample mean ($\bar{E}_K$) and variance (S_K^2) for each zone (Section 3.5.4.6). Then compute the overall area source mean ($\bar{E}$) and variance (S^2) for the total site area using Equations 3-13 and 3-14, respectively. Determine the 95 percent confidence interval for each zone (CI_K) and for the site area (CI) using Equations 3-15 and 3-16.

TABLE 3-3
TOTAL SAMPLE SIZE REQUIRED BASED ON THE PRELIMINARY SAMPLE COEFFICIENT OF VARIATION ESTIMATE*

Coefficient of Variation - CV (%)**	Number of Samples Required (N_K) per Zone K
0 - 19.1	6
19.2 - 21.6	7
21.7 - 24.0	8
24.1 - 26.0	9
26.1 - 28.0	10
28.1 - 29.7	11
29.8 - 31.5	12
31.6 - 33.1	13
33.2 - 34.6	14
34.7 - 36.2	15
36.3 - 37.6	16
37.7 - 38.9	17
39.0 - 40.2	18
40.3 - 41.5	19
41.6 - 42.8	20
42.9 - 43.9	21
44.0 - 45.1	22
45.2 - 46.2	23
46.3 - 47.3	24
47.4 - 48.4	25
48.5 - 49.5	26
49.6 - 50.7	27
50.8 - 51.6	28
51.7 - 52.3	29
52.4 - 53.4	30

*Value given is the sample size required to estimate the average emission rate with 95 percent confidence that the estimate will be within 20 percent of the true mean.

**For CVs greater than 53.4, the sample size required is greater or equal to $CV^2/100$.

3.6 Calibration

3.6.1 Equipment

3.6.1.1 Flow Meters

The flow meter should be calibrated against an NBS-traceable bubble meter before sampling. The flow meter should have a working range of 2-10 L/min.

3.6.1.2 Thermocouple

Fine wire K-type insulated thermocouples are recommended for temperature measurements. Prior to field use, the thermocouple and readout should be calibrated against a mercury-in-glass thermometer meeting ASTM E-1 No. 63C or 63F specifications. The thermocouple should have an accuracy within ±1°C.

3.6.1.3 Calibration Gases

For checking the concentrations of the calibration gases, use calibration gases that are documented traceable to National Bureau of Standard Reference Materials. Use Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors (Protocol Number 1) that is available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Mail Drop 77, Environmental Protection Agency, Research Triangle Park, North Carolina 27711. Obtain a certification from the gas manufacturer that the protocol was followed.

3.6.1.4 Flux Chamber System

Several tests should be performed to characterize a new flux chamber prior to use. These tests should be repeated if a chamber is exposed to severe conditions such as corrosive gases, extremely high levels of organic vapors, or organic liquids.

Blanks

Check the flux chamber for background by placing the chamber over a clean Teflon™ surface and running a test using ultra high purity sweep air and routine operating conditions. Sample collection and analysis should be as previously described (Sections 3.5.2 and 3.5.3).

Recovery Efficiency

Check the flux chamber sample recovery efficiency by placing the chamber over a flat Teflon™ surface containing an inlet port at the center for introduction of a calibration gas(es). The calibration gas should be that used for the on-site analyzer at a concentration of at least 1,000 ppmv (high-level gas). The calibration gas should be introduced into the chamber

at a flow rate of no greater than 0.5 L/min. Add ultra high purity sweep air concurrently through the enclosure sweep air inlet (5 L/min) and determine the concentration exiting the enclosure under routine operating conditions. Compare the measured concentration to the true concentration (corrected for dilution), and calculate a percent recovery using Equation 3-1. Results for a variety of volatile organic compounds are presented in Table 3-1. Results should be within 10 percent of the true concentration. The limited data characterizing the recovery efficiency for halogenated compounds indicate an acceptance level that may be larger than 10 percent.

Corrective Action

If the background levels of the flux chamber are greater than 10 percent of the measured concentrations or 10 ppmv, whichever is smaller, then rerun the blank sample. If high levels persist, then disassemble the flux chamber, clean all internal parts with water and replace those suspected to be contaminated, and reassemble for another blank run. Repeat above until satisfactory levels are reached.

If the recovery efficiency is below 90 percent for non-halogenated compounds, then rerun the recovery test. If low recoveries persist, check for poor sealing and/or inlet gas shortcutting directly from the input line to the exit line and/or misadjusted flow rate settings.

3.6.2 Analyzers

The following procedures should be performed at the recommended frequency during the analysis of flux chamber samples.

3.6.2.1 Real Time

Real-time analyzers are used more for relative, continuous measurements than for absolute measurements. If these analyzers are intended for absolute measurements, then they should be calibrated according to Section 3.6.2.2. Real-time analyzers may be used when data quality requirements are less stringent (Section 3.1.2). As such, these analyzers require less stringent quality control practices.

Each day prior to sampling, a three-point calibration should be performed on each analyzer (Section 3.4.3.1.2). Consider the calibration acceptable if responses are within $\pm$20 percent of the expected response. If the responses are not acceptable, then recalibrate the instrument.

3.6.2.2 Discrete Analyzer

Discrete analyzers are those that are the most relied upon for absolute, quantitative data of the analyzers used on site. As such, these analyzers require more stringent quality control practices (Section 3.1.2). The calibration procedure suggested here is for linear detectors (i.e., FID, PID). Compensations for non-linear detectors used for analysis of sulfonated compounds (flame photometric detectors) must be made.

Prior to each field investigation, a multipoint calibration including zero and at least three upscale concentrations (Subsection 3.4.3.2.2) should be performed to establish the linearity of the analyzer. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of GC response to amount injected (response factor) is a constant over the multipoint range (<10 percent coefficient of variation, standard deviation/mean), linearity through the origin can be assumed, and the average response factor can be used in place of a calibration curve.

Each day prior to sampling and after every fifth sample, the working calibration curve (or response factor) must be verified by the measurement of one or more calibration standards. If the response for any standard varies from the predicted response by 20 percent, the test must be repeated using a fresh calibration standard. If the analyzer response is still unacceptable, a new calibration curve (or response factor) must be prepared for that compound. A new calibration curve (or response factor) should be calculated after each verification of calibration using the acceptable results of the one or more calibration standards injected.

3.7 Quality Control

3.7.1 Sampling Equipment

3.7.1.1 Syringes

Prior to use for sample collection, all syringes should be challenged with one or more of the calibration standards. An acceptable response is within ±10 percent of the predicted response. If the response is unacceptable, then repeat the test. Alternatively, check for leakage around the plunger or lock valve by pressurizing the syringe and submerging it under water. Syringes should be checked after every 25 to 30 uses or whenever leakage is suspected. If Teflon™ tip plungers are used, then suspect memory effects after exposure to high levels of organics. In instances when memory effects are apparent, the Teflon™ tips should be replaced.

3.7.1.2 Gas Canisters

Gas canisters should be cleaned and evacuated before each use. The pressure should be recorded after each evacuation. Prior to sample collection, check the pressure and compare it to that recorded after cleaning. Acceptable differences are <10 percent of the post evacuation pressure. Canisters having unacceptable pressure differences should not be used for sample collection.

To identify gas canisters and record pressure values, each gas canister should have a chain-of-custody form (Figure 3-5). Copies of this form should be retained for the sampler, laboratory, and sample control.

FIGURE 3-5
CHAIN-OF-CUSTODY FORM FOR GAS CANISTER SAMPLES

STAINLESS STEEL CANISTER
CHAIN OF CUSTODY

- - - - - - - - - - - - - TO BE COMPLETED BY FIELD SAMPLER - - - - - - - - - - -

SAMPLE CONTROL NUMBER: _____

CANISTER NUMBER: _____

DATE SAMPLED: _____ TIME: _____

WELL/STATION NUMBER: _____

OVA READING (PEAK): _____

ADDRESS/REFINERY LOCATION: _____

HEIGHT/DEPTH/ROOM: _____

SAMPLER'S INITIALS: _____

TASK: _____

TYPE (CIRCLE ONE): AMBIENT or POINT SOURCE (specify): _____

COMMENTS:

- - - - - - - - - - - - TO BE COMPLETED BY LAB (PART ONE) - - - - - - - - - - -

OPERATION	DATE	INITIALS	COMMENTS
1. Canister cleaned			
2. Filter cleaned			
3. Canister evacuated			Pressure:
4. Canister shipped			
5. Canister received			
6. Analysis completed			
7. Sample discarded			

- - - - - - - - - - - - TO BE COMPLETED BY LAB (PART TWO) - - - - - - - - - - -

PARAMETER	DILUTION 1	DILUTION 2	DILUTION 3	DILUTION 4
Initial Pressure				
Final Pressure				
Add UHP Air				
Dilution Factor				
FINAL Dilution Factor				

3.7.2 Sampling

These tests should be performed at the specified frequency during use of the flux chamber.

3.7.2.1 Sample Blanks

Sample blanks should be performed once daily or after extremely high-level samples. The flux chamber should be cleaned and blanks rerun until exit concentrations are <10 ppmv or <10 percent of expected concentrations, whichever is smaller.

3.7.2.2 Duplicate Samples

A minimum of 10 percent of the sampling points should be sampled in duplicate. Take the two samples over as brief a time span as feasible to minimize any temporal variations in the emitting source.

3.7.2.3 Control Point Samples

One sampling location (grid point or unit) in each zone should be resampled after every ten individual measurements (or a minimum of once per day) when an area source is being investigated. Preferably, this control point should be measured at different times during the diurnal cycle (maximum difference in ambient temperatures). These values provide a measure of temporal variability of the emission rate from the area source.

3.7.3 Analytical

3.7.3.1 Real-Time Analyzers

Real-time measurements are typically made with portable total hydrocarbon analyzers. Real-time analyses are useful for relative measurements (i.e., to determine if steady-state operation of the flux chamber has been attained or to determine the zoning boundaries). Each day following calibration, the analyzer should be challenged with the QC gas (Section 3.4.3.1.3). Analyzer performance should be considered acceptable if the measured concentration is within 20 percent of the certified concentration. If this criterion is not met, the QC analysis should be repeated. If the criterion is still not met, then daily calibration should be repeated.

At the conclusion of each day, the QC gas should be reintroduced to the analyzer. The difference between pretesting and posttesting responses provides a measure of upscale drift. Drifts >30 percent should be flagged and not relied upon. If these data are necessary, then resample the grid points sampled on that day.

3.7.3.2 Discrete Analyzers

Each day after calibration, the analyzer should be challenged with the QC gas (Section 3.4.3.2.3). Analyzer performance should be considered

acceptable if the measured concentration is within 10 percent of the certified concentration. If this criterion is not met, repeat the QC gas analysis. If the criterion still cannot be met, then repeat the daily calibration (Section 3.6.2.2).

At the conclusion of each day's testing, the QC gas and zero grade gas should be reintroduced to the analyzer. The differences between pretesting and posttesting values provide a measure of upscale and zero drifts. Daily drift results that show >20 percent should be flagged and tests repeated if determined necessary.

3.7.3.3 Analysis of Integrated Samples

Quality control for the analysis of integrated samples should include a minimum of 10 percent analytical blanks and 10 percent duplicate analysis. It is recommended that duplicate samples each be analyzed in duplicate to provide information on analytical as well as sampling variation. A convenient technique is the use of a nested sampling scheme as shown in Figure 3-6.

3.8 CALCULATIONS

3.8.1 Definitions

A = surface area enclosed by the flux chamber (0.130 m^2)

a = number of carbon atoms per compound molecule

CI = confidence interval for the area source emission rate mean ($\pm$ug/min·m^2)

CI_K = confidence interval for the zone K emission rate mean ($\pm$ug/min·m^2)

C_{IM} = measured concentration of species I (ppmv) corrected for dilution

C_{IT} = theoretical concentration of species I (ppmv)

C_{KI} = measured concentration for point I in zone K, total NMHC (ppmv-C)

CV_K = coefficient of variance for zone K (%)

$\bar{E}$ = mean emission rate for the area source (ug/min·m^2)

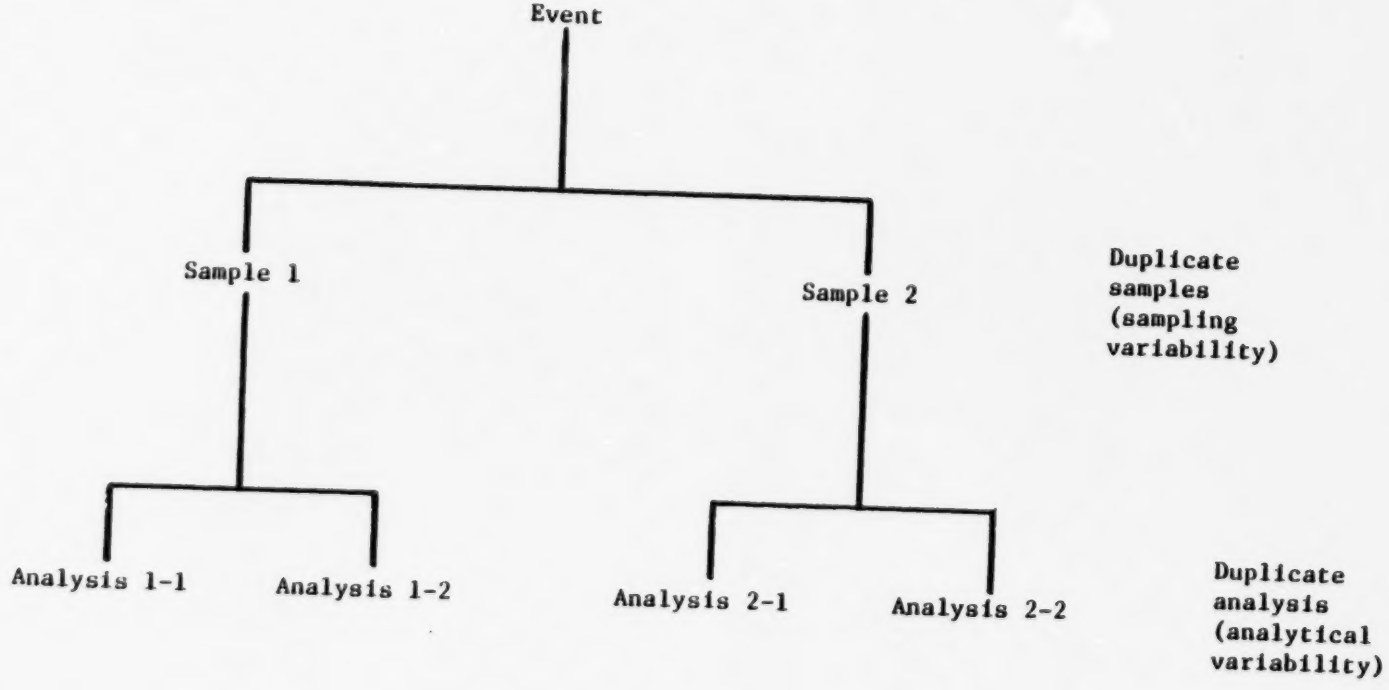
$\bar{E}_K$ = zone K emission rate mean (ug/min·m^2)

E_{KI} = measured emission rate for point I in zone K (ug/min·m^2)

E_{cKI} = measured emission rate for point I in zone K (ug/min·m^2) corrected for temperature variations

MW = molecular weight of compound (g/mole)

FIGURE 3-6
NESTED SAMPLING SCHEME



N = total number of grid points sampled in the area source (all zones)

N_K = final number of grid points (units) sampled in zone K

n_K = initial number of grid points (units) sampled in zone K

P = atmospheric pressure (atm)

Q = sweep air flow rate (L/min)

R = gas constant (0.08205 L·atm/mol·K)

S = standard error of the overall area source emission rate mean ($ug/min \cdot m^2$)

S_K^2 = zone K emission rate variance

T = temperature of laboratory where analyzer is located (K)

TEMP = temperature of the flux chamber air (°C)

$t_{0.025}$ = the 97.5th percentage point of a student's t-distribution (Table 3-4)

V = volume enclosed by the flux chamber (30L)

W_K = the fraction of the site represented by the zone K (zone area (m^2)/site area (m^2))

Y_{KI} = measured concentration for point I in zone K, total NMHC (ug/L)

α = parameter defining the level of confidence $100(1-2\alpha)$ percent

γ = total number of zones in the total area source

ρ = confidence interval (%)

τ = measure of residence time V/Q (min)

3.8.2 Percent Recovery

The percent recovery measurements used to characterize the flux chamber performance are calculated accordingly:

$$\text{Percent Recovery} = (C_{IM}/C_{IT}) \times 100 \qquad (3\text{-}1)$$

where: C_{IM} = the measured concentration of species I (ppmv) corrected for dilution as follows:

$$C_{IM} = (1/DF) \times C \qquad (3\text{-}1a)$$

TABLE 3-4
TABULATED VALUES OF STUDENT'S "t"

Degrees of Freedom*	Tabulated "t" Value**	Degrees of Freedom*	Tabulated "t" Value**
1	12.706	21	2.080
2	4.303	22	2.074
3	3.182	23	2.069
4	2.776	24	2.064
5	2.571	25	2.060
6	2.477	26	2.056
7	2.365	27	2.052
8	2.306	28	2.048
9	2.262	29	2.045
10	2.228	30	2.042
11	2.201	40	2.021
12	2.179	60	2.000
13	2.160	120	1.980
14	2.145	∞	1.960
15	2.131		
16	2.120		
17	2.110		
18	2.101		
19	2.093		
20	2.086		

*Degrees of freedom (df) are equal to the number of samples collected less one.

**Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.05 (the same values are applicable to a one-tailed confidence interval and a probability of 0.025).

where C is the sample concentration (ppmv) and
DF is the dilution factor calculated as follows:

$$S_1/(S_2+S_1) \qquad (3\text{-}1b)$$

where S_1 is the flow rate of the trace gas and
S_2 is the sweep air flow rate

C_{IT} = the true concentration of species I, gas cylinder value (ppmv)

3.8.3 Calculation of the Dilution Factor Involved in Gas Canister Analysis

Analyzing the gas canisters requires pressurizing the canister with nitrogen. This introduces a dilution which must be accounted for as follows:

$$DF = (P_2 - P_1)/(14.7 + P_3) \qquad (3\text{-}2)$$

where: P_1 = the measured pressure after cleaning and canister evacuation prior to sampling (psig)
P_2 = the measured pressure after sample collection (psig)
P_3 = the measured pressure after pressurizing with nitrogen (psig)

The temperature is not required if all pressure measurements used in this equation are performed in the same laboratory (i.e., same temperature) after the canisters have thermally equilibrated.

3.8.4 Area Source Emission Rate Equations

The number of units or grids (n_K) to be sampled per zone (K) is dependent upon the zone area as follows:

$$n_K = 6 + 0.15 \sqrt{\text{area of zone K } (m^2)} \qquad (3\text{-}3)$$

Flux chamber measurements taken at each of the n_K sampling units are measured in terms of ppmv-C. To calculate an emission rate representing the sampled unit, the measured concentration (C_{KI}) must first be converted from ppmv-C to ug/L as follows:

$$Y_{KI} = (P/(R \cdot T))(MW/a)C_{KI} \qquad (3\text{-}4)$$

where P is pressure (atm), R is Rydberg's gas constant (L·atm/mole·K), T is the flux chamber air temperature (K) (Section 3.5.4.5), MW is the species' molecular weight (g/mole), a is the number of moles of carbon per mole, C_{KI} is the measured concentration of sampled unit I in zone K (ppmv-C), and Y_{KI} is the measured concentration of sampled unit I in zone K (ug/L).

The emission rate for point I in zone K (E_{KI}) is then calculated using the converted gas concentration (ug/L) as follows:

$$E_{KI} = (Q \cdot Y_{KI})/A \qquad (3\text{-}5)$$

where Q is the flux chamber sweep air flow rate (L/min), A is the enclosed surface area measured (m^2), and E_{KI} is the emission rate measured for point I in zone K ($ug/m^2 \cdot min$).

Prior to calculating a mean emission rate for the zone measured, the emission rates measured for the individual sampling points need to be corrected for fluctuations in chamber air the temperature (i.e., atmosphere temperature).

The approach used to develop the correction procedure involved developing an empirical equation to predict emission rates as a function of chamber air temperature.(4) The resulting emission rate equation was then used to define the correction factor (C), as follows:

$$C = EF_s/EF_a \qquad (3\text{-}6)$$

where: EF_s = emission factor calculated at the nominal chamber air temperature (Section 3.5.4.5)
EF_a = emission factor calculated at the measured chamber air temperature

Both EF_s and EF_a are predicted using the proper chamber air temperatures and the following equation:

$$EF_{(s \text{ or } a)} = \exp\,[0.013(TEMP_{(s \text{ or } a)})] \qquad (3\text{-}7)$$

where TEMP is measured in °C.

The measured emission rate (EF_{KI}) is then corrected to the nominal emission rate (EF_{cKI}) accordingly:

$$E_{cKI} = C \cdot EF_{KI} \qquad (3\text{-}8)$$

The above procedure has a significance level (i.e., probability that the correlation between chamber air temperature and emission rate measured is due to chance) of 0.4 percent. The standard error of the coefficient in Equation 3-7 is ± 0.003.

The mean emission rate for each zone is then calculated accordingly:

$$\bar{E}_K = \frac{1}{n_K} \sum_{I=1}^{n_K} E_{cKI} \qquad (3\text{-}9)$$

where E_{cKI} is the temperature corrected emission rates (Equation 3-8) and n_K is the number of points sampled in zone K (Section 3.5.4.7).

For each zone (K) sampled, the zone variance (S_K^2) and coefficient of variance (CV_K) must be determined as follows:

$$S_K^2 = \frac{1}{n_K - 1}\left[\sum_{i=1}^{n_K} (E_{cKi}^2) - n_K \bar{E}_K^2\right] \qquad (3\text{-}10)$$

$$CV_K = 100 \cdot S_K/\bar{E}_K \qquad (3\text{-}11)$$

where n_K, E_{cKi}, and $\bar{E}_K$ are defined in Equations 3-3, 3-8, and 3-9, respectively. The standard deviation (S_K) should be calculated for n_K-1 degrees of freedom for populations (n_K) less than or equal to 30. Larger sample sizes require n_K degrees of freedom.

Prior to calculating the overall emission rate that represents all the zones measured, the data must be tested for level of confidence. That is, for the given coefficient of variance (CV_K) of zone K, the zone sample size (n_K) must be equal to or greater than the sample size required (N_K), listed in Table 3-3, to estimate the overall emission rate with 95 percent confidence that the estimate will be within 20 percent of the true mean.

Table 3-3 lists sample sizes required for 95 percent confidence and a 20 percent confidence interval. The total number of samples (N_K) to be collected for different levels of confidences are calculated accordingly:

$$N_K \geq \frac{t_\alpha^2 CV_K^2}{\rho^2} \qquad (3\text{-}12)$$

where a study requires 100(1-2α) percent confidence that the emission rate estimates will be within ρ percent of the true mean. The parameter t_α is the (1-α) percentage point of a student's t-distribution with N_K degrees of freedom. A table of t-values can be found in any book on standard statistical techniques. Recommended values for t_α are listed in Table 3-4.

Use Table 3-3 and CV_K to determine the total number of samples (N_K) required from a given zone. If $N_K > n_K$, then N_K-n_K additional samples must be collected from zone K.

Collect any additional samples and recalculate the emission estimates for the zone mean (E_K) and variance (S_K^2) using Equations 3-9 and 3-10, respectively. If N_K-n_K additional samples were collected, then use N_K samples instead of n_K in the recalculations. The overall area source mean emission rate ($\bar{E}$) is then calculated as follows:

$$\bar{E} = \sum_{K=1}^{\gamma} W_K \cdot \bar{E}_K \qquad (3\text{-}13)$$

where $\bar{E}_K$ is defined by Equation 3-9, W_K is the fraction of site covered by zone K (zone area/site area) and γ is the total number of zones sampled.

Finally, calculate the variance of the overall area source mean (S^2) and the confidence intervals for each zone K (CI_K) and area source (CI) emission rate mean as follows:

$$S^2 = \sqrt{\sum_{K=1}^{\gamma} W_K^2 \cdot S_K^2 / N_K} \qquad (3\text{-}14)$$

$$CI_K = \bar{E}_K \pm t_{0.025} \sqrt{S_K^2 / N_K} \qquad (3\text{-}15)$$

$$CI = \bar{E} \pm t_{0.025} \cdot S \qquad (3\text{-}16)$$

SECTION 4

CASE STUDY

To supplement the protocol presented in Section 3, a case study will be reviewed. This study will illustrate an actual application of the protocol. Calculations and pertinent decisions will be presented.

The site, referred to as the Bonifay Spill Site, was the scene of an accidental spill of 5500 gallons of JP-4 aviation fuel. The spill site occurred near the intersection of two roads. The majority of the contaminated soil was excavated. The residual product extended over two areas, 30 feet of unvegetated right-of-way along the highway and into a pine forest containing dense underbrush.

The free surface of the water table was three feet below the land surface. The thickness of the unconsolidated sediments that comprised the water table aquifer at the site ranged from 20 to 50 feet. The state aquifer underlaid this sediment layer. Contamination of the free water table surface was expected since it was only 3 feet below landsurface. However, the state aquifer was not considered threatened due to the contaminants net upward hydraulic gradient.

A preliminary survey was performed to define the contaminated area. A series of ten borings indicated that the contaminants had percolated downward to the capillary fringe and moved laterally down gradient. A lens of product several inches thick was detected at a depth of seven feet below land surface. The estimated extent of contamination at the time of the survey study was 7,000 square feet (Figure 4-1).

Results from a preliminary emissions survey performed with a portable real-time analyzer (organic vapor analyzer) held a few inches above ground were used to divide the area source into emission zones for gridding purposes. The survey indicated only one zone was present, and the site was gridded accordingly. The field data for the survey is shown in Table 4-1. The grid system used is shown in Figure 4-2.

Surface emission measurements were made initially at eight sampling grid points. The protocol, at that time, called for the minimum number of sampling points per zone, n_K, to be selected according to the following equation (note, this equation has since been changed to Equation 3-3).

$$n_K \geq 6 + 0.1\sqrt{\text{zone area } (m^2)}$$

FIGURE 4-1
SCHEMATIC DIAGRAM OF BONIFAY SPILL SITE, MONITOR WELLS, AND EXPLORATORY BORINGS (BROWN AND KIRKNER, INC., 1983)

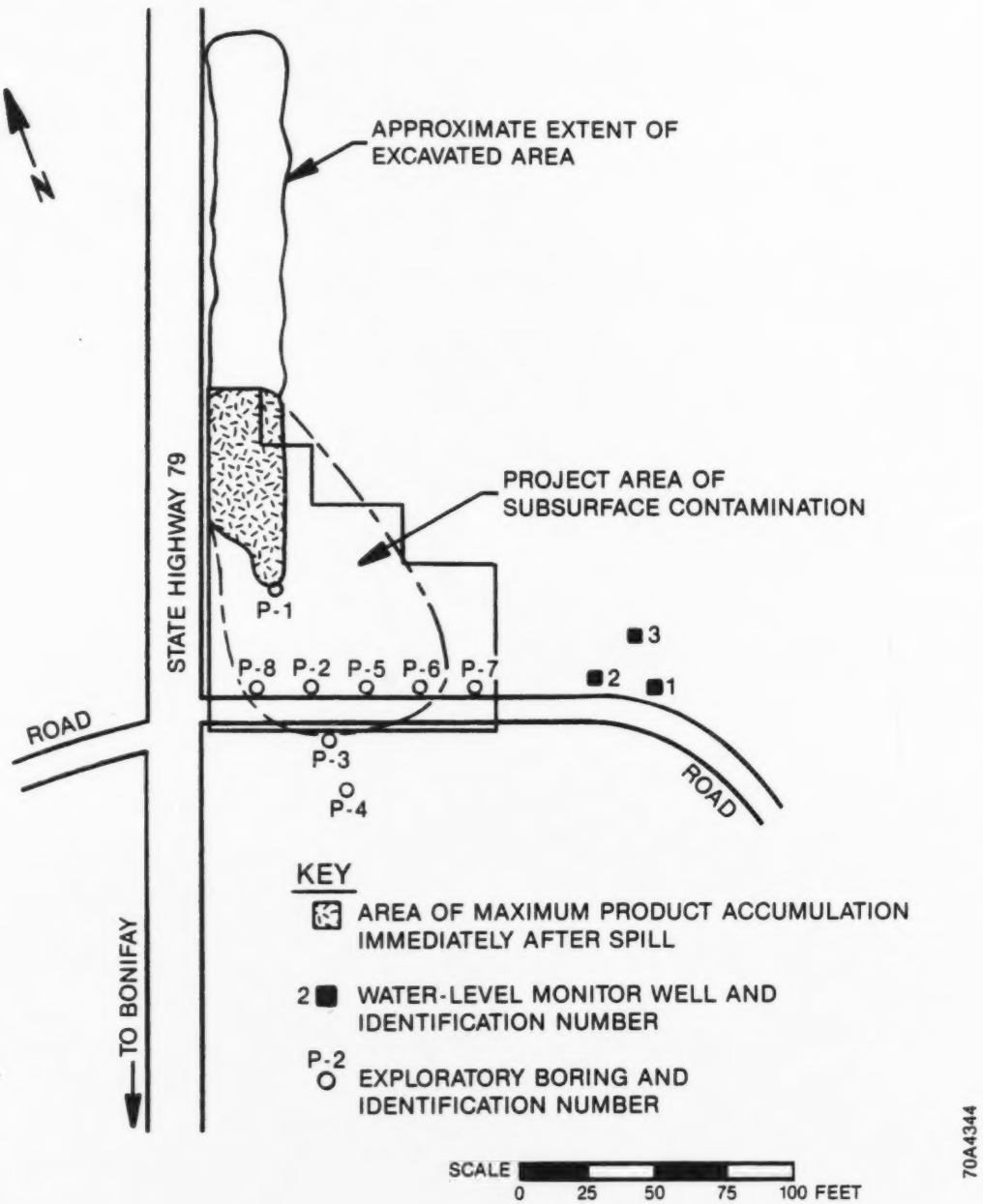


TABLE 4-1
FIELD DATA SHEET FOR UNDISTURBED SURFACE SURVEY

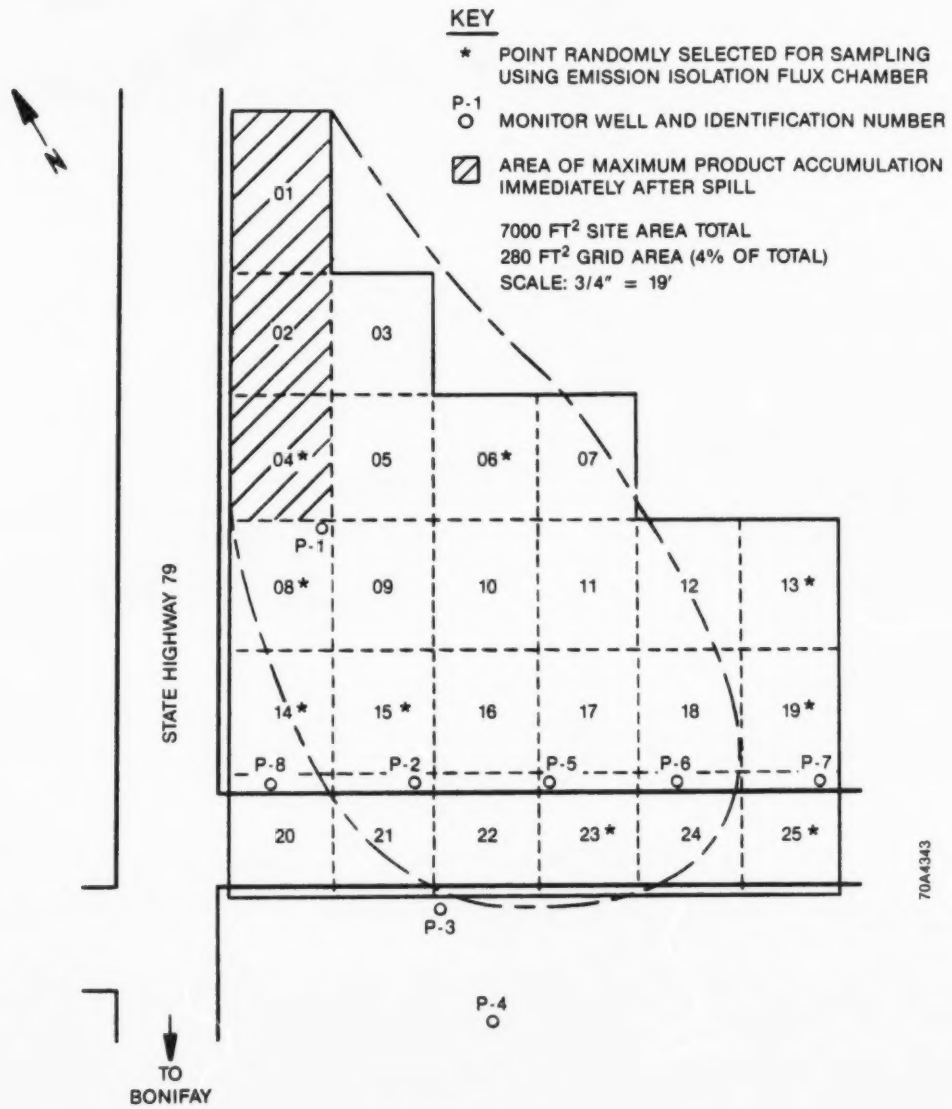
Operator: BME Date: 1-12-84

Weather: Temperature = 45°F. Light breeze, partly cloudy

Grid Point	Surface Temperature	Air Temperature	GC-PID Peak (ppmv)	GC-PID Average (ppmv)	Comment
01	40-42	45°F		0.10	Sampler was 2"-6"
02				0.10	above soil surface
04				0.10	
08				0.10	
14				0.10	
20				0.10-0.12	
21				0.10-0.12	
22				0.10-0.12	
23				0.10-0.12	
24				0.10-0.12	
25				0.10-0.12	
16				0.10	
18				0.10	
19				0.10	
Well P-3				5-6	
Well P-4			25	7	
Well P-7				40-70	
Well P-7				65	Measurement on 1/14/84 (with GC-FID)

Comments: Survey done at Midday. Results indicate only one zone

FIGURE 4-2
SCHEMATIC DIAGRAM OF SAMPLING GRID AT BONIFAY SPILL SITE



For the single zone at Bonifay, this reduced to:

$$n_K \geq 6 + 0.1 \sqrt{650\ m^2} = 8.5$$

The 8 locations were selected through the use of a random number table, Appendix A. Grid point 08 was selected to be the control point (i.e., a sampling point to be repeated each day) since it was believed that emissions would be of the largest magnitude at that location. At each sampling location a gas syringe sample was taken for on-site analysis. At several sampling locations, a gas canister was collected in addition to the syringe samples for off-site detailed analysis. A sample field data sheet is shown in Figure 4-3. The results of the emission rate measurement are given in Table 4-2, and a sample calculation is given in Table 4-3.

Total non-methane emission rates were calculated for each grid point based on the on-site analytical data. These emission rates are also presented in Table 4-2. The variation (spatially and temporally) in measured emission rates over the extent of the contaminated area was large (93.8 percent coefficient of variation). Replicate sampling at the control point allowed an estimate of the emission rate temporal variability. The temporal variability was also large (96.0 percent). The major contributor to the variation in measured emission rates from point-to-point can, therefore, be attributed to day-to-day (temporal) variability. The spatial variability was then estimated to be negligible. Using Table 3-3 to determine the total number (N_K) of samples to be collected based upon the spatial variability shows that at least 17 samples should have been collected. Although additional samples were required to be collected, sampling was terminated due to rain. It was realized that the lack of a complete data set would then result in a larger emission rate confidence interval.

Using the following equation, the 95 percent confidence interval (CI) for the zone emission rate was estimated.

$$CI = ER \pm t_{0.025}\sqrt{s^2/N_K}$$

where ER is the mean emission rate of the zone, s^2 is the zone variance, N_K is the total number of sites sampled, and $t_{0.025}$ is obtained from Table 3-4. The 95 percent confidence interval for the zone emission rate is from 11.3 $ug/min \cdot m^2$ to 55.2 $ug/min \cdot m^2$.

FIGURE 4-3
FIELD DATA SHEET FOR ISOLATION FLUX CHAMBER SAMPLING AT GRID POINT 08

Date 1-13-84 Samplers BME

Location Bonifay Spill Site, Grid Point 08

Concurrent Activity None

Surface Description Sand

Time	Purge Air or Flowrate	Residence Time Number (τ)	Temp. °F		Gas Data		Air Sample Number
			Surface	Air	OVA ppmv	HNU ppmv	
0858	4.86 L/min	0	46	48	-	0.15	
0902	4.86 L/min	1			-	0.16	
0906	4.86 L/min	2			-	0.16	
0910	4.86 L/min	3			4.0	0.16	
0914	4.86 L/min	4			4.0	-	
0918	4.86 L/min	5			-	-	Canister B003
0933	4.86 L/min	9			4.0	0.16	Gas Syringe B002

Comments OVA background = 4 ppm. Some trouble with syringe needle plugging

TABLE 4-2
RESULTS OF GC ANALYSIS OF GAS SYRINGE TAKEN DURING FLUX CHAMBER SAMPLING

Grid Point	Sample No.	Date	Total NMHC Syringe (ppmv-C)	Total NMHC Syringe (ug/L)	Sweep Air Rate (L/min)	Atmospheric Temperature °F	Atmospheric Temperature °C	Average Emission Rate ($ug/m^2 \cdot min$)
4	B004	1/13/84	1.0	0.62	2.60	47	8.3	14.4
6	B017-A	1/14/84	6.8	4.2	2.60	51*	10.6	72.6
8	B001	1/12/84	2.0	1.2	5.00	42	5.5	79.6
8	B002	1/13/84	1.0	0.62	4.86	48	8.9	24.9
8	B016	1/14/84	1.0	0.62	2.60	52	11.1	10.0
14	B006	1/13/84	1.0	0.62	2.60	45	7.2	16.6
15	B013	1/13/84	1.0	0.62	2.60	51	10.6	10.7
19	B009	1/13/84	1.0	0.62	2.60	51	10.6	10.7
23	B011	1/13/84	1.0	0.62	2.60	50	10.0	11.5
25	B008	1/13/84	8.8	5.4	2.60	53	11.7	81.4

Variability

Spatial and Temporal:	
Mean	33.24
Standard Deviation	31.17
CV(%)	93.8
Temporal: (Control Point 8)	
Mean	38.2
Standard Deviation	36.6
CV(%)	96.0

*Surface temperature used rather than the chamber air temperature due to a large temperature differential not present in the other measurements. This is suggestive of an error in chamber air temperature measurement.

TABLE 4-3
SAMPLE CALCULATIONS OF THE EMISSION RATE FOR GRID POINT 08 ON 1/13/84

Concentration Conversion:

$$Y_I = (P/(R \cdot T))(MW/a)(C_I) \qquad \text{(Equation 3-4)}$$

where: P = 1 atm
R = 0.08205 L·atm/mole·K
T = 282.6K (average area site air temperature)
MW = 86.18 g/mole (referenced to hexane)
a = 6 moles of carbon/mole of hexane
C_I = 1.0 ppmv-C

$$Y_I = \frac{1 \text{ atm}}{(0.08205 \text{ L·atm/mole·K})(282.6\text{K})} \times \frac{86.18 \text{ g/mole}}{6 \text{ mole C/mole}} \times 1.0 \text{ ppmv-C}$$

$$Y_I = 0.6194 \text{ ug/L}$$

Emission Rate (uncorrected)

$$E_I = (Q \cdot Y_I)/A \qquad \text{(Equation 3-5)}$$

where: Q = 4.86 L/min
Y_I = 0.6194 ug/L
A = 0.130 m^2

$$E_I = \frac{4.86 \text{ l/min} \cdot 0.6194 \text{ ug/L}}{0.130 \text{ m}^2}$$

$$E_I = 23.15 \text{ ug/min} \cdot \text{m}^2$$

Emission Rate Correction Factor

$$EF_S = \exp[0.13(TEMP_S)] \qquad \text{(Equation 3-7)}$$

where: $TEMP_S$ = 9.45°C (nominal chamber air temperature °C)
EF_S = emission factor at nominal chamber air temperature

$$EF_S = \exp(0.13 \cdot 9.45)$$
$$EF_S = 3.416$$

(Continued)

TABLE 4-3
(Continued)

$EF_a = \exp[0.13(TEMP_a)]$

where: $TEMP_a$ = 8.9°C (measured chamber air temperature °C)
EF_a = emission factor at the measured chamber air temperature.

$EF_a = \exp(0.13 \cdot 8.9)$
$EF_a = 3.180$

$C = EF_s/EF_a$ (Equation 3-6)
$C = 3.416/3.180$
$C = 1.074$

Emission Rate (corrected for temperature variation)

$E_{cl} = C \cdot E_l$ (Equation 3-8)
$E_{cl} = 1.074 \cdot 23.15$ ug/min·m^2
$= 24.86$
$= 24.9$ ug/min·m^2

SECTION 5

ADDITIONAL INFORMATION

For further information on vapor/liquid equilibria (VLE) for organic systems, the following reference is suggested. The intent of this bibliography was to provide a ready listing of the references for data on VLE.

Nelson, T.P., N.P. Meserole, Annotated Bibliography of Published Material on Vapor/Liquid Equilibria. EPA, July 1983.

For further information on the selection of the flux chamber enclosure method for direct measurement of gas emission rates from contaminated soils and/or groundwater, the following reference is suggested.

Radian Corporation. Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Interim Report. EPA Contract No. 68-02-3513, Work Assignment 32, August 1983.

For further information on the actual field applications of this technique, the following references are suggested:

Radian Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment: Tustin Spill Site Data Volume. EPA Contract No. 68-02-3513, Work Assignment 32. July 27, 1984.

Radian Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Bonifay Spill Site Data Volume. EPA Contract No. 68-02-3513, Work Assignment 32, 1984.

For further information on the validation of the flux chamber technique for emission rate measurements on soil surfaces, the following reference is suggested:

Kienbusch, M.R., D. Ranum, Validation of Flux Chamber Emission Measurements on Soil Surfaces. EPA Contract No. 68-02-3889, Work Assignment 18, December 1985.

For information concerning the emission process including diffusion and adsorption, the following reference is suggested:

Manos, C.G., Jr., Effects of Clay Mineral Organic Matter Complexes on VOC Adsorption, Draft Report. EPA Contract No. 68-02-3889, Work Assignment 18, October 3, 1985.

Radian Corporation. Soil Gas Sampling Techniques of Chemicals for Exposure Assessment; Laboratory Study of Emission Rates from Soil Columns, Draft Final Report. EPA Contract No. 68-02-3513, Work Assignment 32, October 1984.

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1. Farmer, W.J., M.S. Yang, and J. Letey. Land Disposal of Hexachlorobenzene Wastes--Controlling Vapor Movement in Soil. EPA-600/2-80-119, Municipal Environmental Research Laboratory, Cincinnati, Ohio, August 1981.

2. Shen, T.T. Estimating Hazardous Air Emissions from Disposal Sites, Pollution Engineering, August 1981.

3. U.S. EPA, Office of Solid Waste. Guidance Document for Subpart F, Air Emission Monitoring, Land Disposal Toxic Air Emissions Evaluation Guideline. December 1980.

4. Kienbusch, M.R, D. Ranum. Validation of Flux Chamber Emission Measurements on Soil Surfaces. EPA, EMSL, Contract No. 68-02-3889, Work Assignment 18, December 1985.

5. Radian Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Interim Report, EPA Contract No. 68-02-3513, Work Assignment 32, U.S. EPA EMSL, EAD, August 1983.

6. Adams, D.F., M.R. Pack, W.L. Bamesberger, and A.E. Sherrard, "Measurement of Biogenic Sulfur-Containing Gas Emissions from Soils and Vegetation." In: Proceedings of 71st Annual APCA Meeting, Houston, TX, 1978, p. 78-76.

7. Adams, D.F., Sulfur Gas Emissions from Flue Gas Desulfurization Sludge Ponds. J. Air Pol. Contr. Assoc. Vol. 29, No. 9, p. 963-968, 1979.

8. Denmead, O.T. Chamber Systems for Measuring Nitrous Oxide Emission from Soils in the Field. Soil Sciences Soc. of Am. J., 43, p. 89-95, 1979.

9. Balfour, W.D. and C.E. Schmidt, Sampling Approaches for Measuring Emission Rates from Hazardous Waste Disposal Facilities. In: Proceedings of 77th Annual Meeting of the Air Pollution Control Association, San Francisco, California, June 1984.

10. Zimmerman, P. Procedures for Conducting Hydrocarbon Emission Inventories of Biogenic Sources and Some Results of Recent Investigations. In: Proceedings of 1977 Environmental Protection Agency Emission Inventory/Factor Workshop, Raleigh, NC, 1977.

APPENDIX A

SELECTION OF A RANDOM SAMPLE

An illustration of the method of use of tables of random numbers follows. Suppose the population consists of 87 items, and we wish to select a random sample of 10. Assign to each individual a separate two-digit number between 00 and 86. In a table of random numbers, pick an arbitrary starting place and decide upon the direction of reading the numbers. Any direction may be used, provided the rule is fixed in advance and is independent of the numbers occurring. Read two-digit numbers from the table, and select for the sample those individuals whose numbers occur until 10 individuals have been selected. For example, in Table A-1, start with the second page of the table, column 20, line 6, and read down. The 10 items picked for the sample would thus be numbers 38, 44, 13, 73, 39, 41, 35, 07, 14, and 47.

The method described is applicable for obtaining simple random samples from any sampled population consisting of a finite set of individuals. In the case of an infinite sampled population for the target population of weighings as comprising all weighings which might conceptually have been made during the time while weighing was done. We cannot, by mechanical randomization, draw a random sample from this population, and so must recognize that we have a random sample only <u>by assumption</u>. This assumption will be warranted if previous data indicate that the weighing procedure is in a state of statistical control; unwarranted if the contrary is indicated; and a leap in the dark if no previous data are available.

TABLE A-1
SHORT TABLE OF RANDOM NUMBERS

46	96	85	77	27	92	86	26	45	21	89	91	71	42	64	64	58	22	75	81	74	91	48	46	18
44	19	15	32	63	55	87	77	33	29	45	00	31	34	84	05	72	90	44	27	78	22	07	62	17
34	39	80	62	24	33	81	67	28	11	34	79	26	35	34	23	09	94	00	80	55	31	63	27	91
74	97	80	30	65	07	71	30	01	84	47	45	89	70	74	13	04	90	51	27	61	34	63	87	44
22	14	61	60	86	38	33	71	13	33	72	08	16	13	50	56	48	51	29	48	30	93	45	66	29
40	03	96	40	03	47	24	60	09	21	21	18	00	05	86	52	85	40	73	73	57	68	36	33	91
52	33	76	44	56	15	47	75	78	73	78	19	87	06	98	47	48	02	62	03	42	05	32	55	02
37	59	20	40	93	17	82	24	19	90	80	87	32	74	59	84	24	49	79	17	23	75	83	42	00
11	02	55	57	48	84	74	36	22	67	19	20	15	92	53	37	13	75	54	89	56	73	23	39	07
10	33	79	26	34	54	71	33	89	74	68	48	23	17	49	18	81	05	52	85	70	05	73	11	17
67	59	28	25	47	89	11	65	65	20	42	23	96	41	64	20	30	89	87	64	37	93	36	96	35
93	50	75	20	09	18	54	34	68	02	54	87	23	05	43	36	98	29	97	93	87	08	30	92	98
24	43	23	72	80	64	34	27	23	46	15	36	10	63	21	59	69	76	02	62	31	62	47	60	34
39	91	63	18	38	27	10	78	88	84	42	32	00	97	92	00	04	94	50	05	75	82	70	80	35
74	62	19	67	54	18	28	92	33	69	98	96	74	35	72	11	68	25	08	95	31	79	11	79	54
91	03	35	60	81	16	61	97	25	14	78	21	22	05	25	47	26	37	80	39	19	06	41	02	00
42	57	66	76	72	91	03	63	48	46	44	01	33	53	62	28	80	59	55	05	02	16	13	17	54
06	36	63	06	15	03	72	38	01	58	25	37	66	48	56	19	56	41	29	28	76	49	74	39	50
92	70	96	70	89	80	87	14	25	49	25	94	62	78	26	15	41	39	48	75	64	69	61	06	38
91	08	88	53	52	13	04	82	23	00	26	36	47	44	04	08	84	80	07	44	76	51	52	41	59
68	85	97	74	47	53	90	05	90	84	87	48	25	01	11	05	45	11	43	15	60	40	31	84	59
59	54	13	09	13	80	42	29	63	03	24	64	12	43	28	10	01	65	62	07	79	83	05	59	61
39	18	32	69	33	46	58	19	34	03	59	28	97	31	02	65	47	47	70	39	74	17	30	22	65
67	43	31	09	12	60	19	57	63	78	11	80	10	97	15	70	04	89	81	78	54	84	87	83	42
61	75	37	19	56	90	75	39	03	56	49	92	72	95	27	52	87	47	12	52	54	62	43	23	13
78	10	91	11	00	63	19	63	74	58	69	03	51	38	60	36	53	56	77	06	69	03	89	91	24
93	23	71	58	09	78	08	03	07	71	79	32	25	19	61	04	40	33	12	06	78	91	97	88	95
37	55	48	82	63	89	92	59	14	72	19	17	22	51	90	20	03	64	96	60	48	01	95	44	84
62	13	11	71	17	23	29	25	13	85	33	35	07	69	25	68	57	92	57	11	84	44	01	33	66
29	89	97	47	03	13	20	86	22	45	59	98	64	53	89	64	94	81	55	87	73	81	58	46	42
16	94	85	82	89	07	17	30	29	89	89	80	98	36	25	36	53	02	49	14	34	03	52	09	20
04	93	10	59	75	12	98	84	60	93	68	16	87	60	11	50	46	56	58	45	88	72	50	46	11
95	71	43	68	97	18	85	17	13	08	00	50	77	50	46	92	45	26	97	21	48	22	23	08	32
86	05	39	14	35	48	68	18	36	57	09	62	40	28	87	08	74	79	91	08	27	12	43	32	03
59	30	60	10	41	31	00	69	63	77	01	89	94	60	19	02	70	88	72	33	38	88	20	60	86
05	45	35	40	54	03	98	96	76	27	77	84	80	08	64	60	44	34	54	24	85	20	85	77	32
71	85	17	74	66	27	85	19	55	56	51	36	48	92	32	44	40	47	10	38	22	52	42	29	96
80	20	32	80	98	00	40	92	57	51	52	83	14	55	31	99	73	23	40	07	64	54	44	99	21
13	50	78	02	73	39	66	82	01	28	67	51	75	66	33	97	47	58	42	44	88	09	28	58	06
67	92	65	41	45	36	77	96	46	21	14	39	56	36	70	15	74	43	62	69	82	30	77	28	77
72	56	73	44	26	04	62	81	15	35	79	26	99	57	28	22	25	94	80	62	95	48	98	23	86
28	86	85	64	94	11	58	78	45	36	34	45	91	38	51	10	68	36	87	81	16	77	30	19	36
69	57	40	80	44	94	60	82	94	93	98	01	48	50	57	69	60	77	69	60	74	22	05	77	17
71	20	03	30	79	25	74	17	78	34	54	45	04	77	42	59	75	78	64	99	37	03	18	03	36
89	98	55	98	22	45	12	49	82	71	57	33	28	69	50	59	15	09	25	79	39	42	84	18	70
58	74	82	81	14	02	01	05	77	94	65	57	70	39	42	48	56	84	31	59	18	70	41	74	60
50	54	73	81	91	07	81	26	25	45	49	61	22	88	41	20	00	15	59	93	51	60	65	65	63
49	33	72	90	10	20	65	28	44	63	95	86	75	78	69	24	41	65	86	10	34	10	32	00	93
11	85	01	43	65	02	85	69	56	88	34	29	64	35	48	15	70	11	77	83	01	34	82	91	04
34	22	46	41	84	74	27	02	57	77	47	93	72	02	95	63	75	74	69	69	61	34	31	92	13

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05	57	23	06	26	23	08	66	16	11	75	28	81	56	14	62	82	45	65	80	36	02	76	55	63
37	78	16	06	57	12	46	22	90	97	78	67	39	06	63	60	51	02	07	16	75	12	90	41	16
23	71	15	08	82	64	87	29	01	20	46	72	05	80	19	27	47	15	76	51	58	67	06	80	54
42	67	98	41	67	44	28	71	45	08	19	47	76	30	26	72	33	69	92	51	95	23	26	85	76
05	83	03	84	32	62	83	27	48	83	09	19	84	90	20	20	50	87	74	93	51	62	10	23	30
60	46	18	41	23	74	73	51	72	90	40	52	95	41	20	89	48	98	27	38	81	33	83	82	94
32	80	64	75	91	98	09	40	64	89	29	99	46	35	69	91	50	73	75	92	90	56	82	93	24
79	86	53	77	78	06	62	37	48	82	71	00	78	21	65	65	88	45	82	44	78	93	22	78	09
45	13	23	32	01	09	46	36	43	66	37	15	35	04	88	79	83	53	19	13	91	59	81	81	87
20	60	97	48	21	41	84	22	72	77	99	81	83	30	46	15	90	26	51	73	66	34	99	40	60
67	91	44	83	43	25	56	33	28	80	99	53	27	56	19	80	76	32	53	95	07	53	09	61	98
86	50	76	93	86	35	68	45	37	83	47	44	92	57	66	59	64	16	48	39	26	94	54	66	40
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90	24	83	48	07	41	56	68	11	14	77	75	48	68	08	90	89	63	87	00	06	18	63	21	91
98	98	97	42	27	11	80	51	13	13	03	42	91	14	51	22	15	48	67	52	09	40	34	60	85
74	20	94	21	49	96	51	69	99	85	43	76	55	81	36	11	88	68	32	43	08	14	78	05	34
94	67	48	87	11	84	00	85	93	56	43	99	21	74	84	13	56	41	90	96	30	04	19	68	73
58	18	84	82	71	23	66	33	19	25	65	17	90	84	24	91	75	36	14	83	86	22	70	86	89
31	47	28	24	88	49	28	69	78	62	23	45	53	38	78	65	87	44	91	93	91	62	76	09	20
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69	37	22	23	46	10	75	83	62	94	44	65	46	23	65	71	69	20	89	12	16	56	61	70	41
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37	07	47	79	60	75	24	15	31	63	25	93	27	66	19	53	52	49	98	45	12	12	06	00	32
72	08	71	01	73	46	39	60	37	58	22	25	20	84	30	02	03	62	68	58	38	04	06	89	94
55	22	48	46	72	50	14	24	47	67	84	37	32	84	82	64	97	13	69	86	20	09	80	46	75
69	24	98	90	70	29	34	25	33	23	12	69	90	50	38	93	84	32	28	96	03	65	70	90	12
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51	40	94	06	80	61	34	28	46	28	11	48	48	94	60	65	06	63	71	06	19	35	05	32	56
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33	75	88	51	00	33	56	15	84	34	28	50	16	65	12	81	56	43	54	14	63	37	74	97	59
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22	21	13	16	10	52	57	71	40	49	95	25	55	36	95	57	25	25	77	05	38	05	62	57	77
97	94	83	67	90	68	74	88	17	22	38	01	04	33	49	38	47	57	61	87	15	39	43	87	00
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29	95	61	42	65	05	72	27	28	18	09	85	24	59	46	03	91	55	38	62	51	71	47	37	38
81	96	78	90	47	41	38	36	33	95	05	90	26	72	85	23	23	30	70	51	56	93	23	84	80
44	62	20	81	21	57	57	85	00	47	26	10	87	22	45	72	03	51	75	23	38	38	56	77	97
68	91	12	15	08	02	18	74	56	79	21	53	63	41	77	15	07	39	87	11	19	25	62	19	30
29	33	77	60	29	09	25	09	42	28	07	15	40	67	56	29	58	75	84	06	19	54	31	16	53
54	13	39	19	29	64	97	73	71	61	78	03	24	02	93	86	69	76	74	28	08	98	84	08	23
75	16	85	64	64	93	85	68	08	84	15	41	57	84	45	11	70	13	17	60	47	80	10	13	00
36	47	17	08	79	03	92	85	18	42	95	48	27	37	99	98	81	94	44	72	06	95	42	31	17
29	61	08	21	91	23	76	72	84	98	26	23	66	54	86	88	95	14	82	57	17	99	16	28	99

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03	46	38	56	84	81	20	89	68	52	45	41	01	71	55	14	18	05	18	01	74	94	50	66	07
74	12	14	57	26	12	48	83	67	04	88	69	05	27	23	68	84	23	52	07	21	67	13	52	01
08	23	73	51	23	92	93	05	54	32	84	46	61	33	92	13	30	91	73	11	30	44	21	71	20
99	21	30	24	79	30	18	06	96	20	62	06	47	96	07	04	82	93	01	56	62	70	43	22	85
96	82	59	39	23	22	20	95	72	00	24	85	63	57	75	88	05	79	13	75	78	64	25	89	85
62	16	18	23	64	50	90	57	50	54	04	96	09	08	17	14	63	17	80	80	56	10	17	11	57
21	40	82	41	45	41	41	89	46	18	55	86	94	32	57	44	12	64	75	12	78	01	13	69	81
13	83	48	82	60	78	96	30	57	13	40	28	10	24	48	73	50	92	70	18	72	86	54	09	76
29	65	33	93	92	99	26	01	86	11	85	42	48	86	59	24	96	35	07	87	67	31	25	89	62
17	49	05	12	13	58	01	98	80	17	83	35	38	14	79	82	83	56	44	51	35	40	70	68	22
14	36	47	29	15	14	22	27	62	93	15	60	43	13	05	25	75	40	08	85	44	70	89	64	13
78	09	76	61	07	48	31	27	48	28	96	11	26	95	03	06	86	81	52	72	66	74	71	60	25
83	17	94	26	39	01	48	68	56	97	05	76	82	89	15	66	81	63	81	96	12	44	71	57	43
87	12	89	46	85	58	09	94	39	92	09	08	76	54	88	82	73	24	94	39	02	79	07	58	27
44	30	30	40	85	96	34	99	87	03	93	03	00	74	18	67	13	97	11	12	59	30	54	51	66
54	56	85	50	81	32	42	53	60	36	98	03	65	10	60	26	52	64	74	35	28	13	24	65	23
65	99	30	88	88	44	91	22	50	72	61	95	90	98	80	65	03	45	04	27	88	70	88	40	49
55	56	01	94	09	94	02	71	85	10	27	20	51	27	86	09	15	11	62	41	03	22	82	10	60
55	78	63	40	57	16	20	17	73	02	76	09	62	95	85	67	75	45	99	63	59	55	88	27	99
83	78	98	57	23	38	95	61	06	58	69	07	35	82	10	35	61	61	66	06	75	45	83	33	70
20	14	56	25	85	78	33	37	34	15	50	63	78	74	56	49	84	72	58	00	93	68	11	47	46
48	04	07	78	13	43	03	62	46	20	06	94	09	27	69	00	71	51	43	84	21	12	86	03	51
61	10	14	39	57	87	76	60	77	02	06	50	15	60	46	22	27	52	87	43	69	58	65	79	02
64	91	36	96	42	22	57	18	13	44	46	81	95	15	37	91	81	63	33	38	39	50	47	45	94
89	53	11	10	33	10	46	41	63	84	20	46	86	41	05	82	95	56	76	23	03	13	94	28	49
96	45	86	42	40	85	95	17	28	74	65	20	70	90	34	33	61	11	01	31	37	28	81	00	31
84	11	25	39	49	31	80	86	53	51	35	48	22	28	25	27	06	38	71	90	50	77	40	41	58
29	75	56	28	39	23	26	12	23	48	89	28	34	08	52	21	05	73	08	04	83	42	91	01	91
68	92	40	32	19	49	20	85	32	69	34	17	99	11	56	39	15	67	55	53	65	29	15	51	32
94	19	67	99	27	70	71	04	43	18	44	18	75	11	70	53	21	60	78	30	92	54	21	02	42
86	84	68	46	85	58	91	23	65	24	71	19	67	18	79	90	83	47	86	32	48	69	97	10	87
63	22	84	35	10	02	05	03	47	93	45	70	25	27	90	32	98	41	45	96	39	88	91	78	79
42	53	20	46	19	11	16	93	21	93	14	91	74	92	31	97	68	24	20	35	19	54	75	37	84
37	90	76	51	58	49	25	58	28	69	55	55	73	10	22	66	79	23	80	03	51	11	00	81	37
20	12	97	40	25	45	94	35	18	65	10	99	31	24	42	14	53	78	41	79	36	57	79	19	76
24	11	65	19	92	46	11	76	64	37	33	23	96	23	73	93	99	53	14	49	40	01	63	17	74
98	21	62	16	29	73	52	06	26	35	30	52	74	61	20	57	45	86	36	54	75	29	64	49	43
02	82	14	07	19	72	77	97	39	77	25	32	60	39	04	04	88	65	47	20	81	72	40	65	48
97	20	87	54	01	93	38	53	07	38	61	00	22	95	65	79	69	26	90	49	24	61	78	19	40
17	86	31	34	32	29	40	23	66	71	14	91	93	75	02	10	13	86	27	32	59	36	40	06	61
75	50	70	16	34	21	99	87	09	37	27	40	66	07	73	13	44	06	10	43	91	11	73	13	97
47	53	77	58	88	52	47	37	21	60	83	58	21	59	82	88	05	35	17	66	33	62	15	09	88
20	93	99	76	58	93	00	39	77	75	59	39	49	61	13	68	11	80	07	72	81	65	95	94	53
91	02	65	18	16	57	93	64	76	45	21	49	51	58	96	12	62	42	10	79	57	44	97	35	66
58	49	25	97	76	12	90	94	85	25	36	40	97	46	71	83	36	55	41	38	49	98	82	70	96
98	51	20	13	77	75	86	22	62	68	36	87	02	47	99	68	80	27	34	10	09	22	84	59	33
05	32	54	17	31	87	20	77	78	80	98	42	48	42	47	41	76	11	41	79	41	48	26	94	59
40	96	49	91	79	57	18	61	50	48	06	07	68	43	07	01	04	06	22	03	11	11	75	95	02
58	43	93	93	53	01	61	75	76	90	25	97	08	76	69	35	65	24	83	85	00	49	37	05	46
76	98	86	43	60	47	85	65	73	62	66	15	98	17	20	43	96	27	87	53	57	37	92	86	46

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24	81	06	14	98	24	93	58	63	66	58	26	24	45	65	91	42	68	67	42	61	74	77	93	46
75	55	54	29	67	02	81	01	67	54	08	81	34	00	79	62	38	52	14	88	38	66	59	41	97
49	71	80	54	37	73	34	11	74	14	91	86	82	41	02	76	12	36	71	38	43	72	84	36	27
04	19	48	35	54	98	00	41	47	44	63	13	27	50	18	75	16	72	40	90	02	45	87	82	15
66	15	52	42	22	91	22	96	38	41	03	27	15	67	26	36	81	75	11	82	94	33	62	08	94
10	80	17	67	83	05	31	23	08	07	40	00	60	44	65	70	16	31	73	05	46	41	47	64	68
40	42	27	55	76	82	88	42	76	51	58	49	58	75	38	23	57	06	64	69	46	90	09	55	68
95	57	21	21	25	12	05	41	70	28	03	59	97	37	64	48	69	48	59	60	89	76	35	83	05
57	27	64	94	98	88	93	70	86	59	46	84	08	32	31	75	61	19	49	11	28	46	76	79	28
80	56	69	49	63	83	78	78	76	36	89	51	16	47	35	86	69	96	69	88	91	22	47	24	84
44	51	75	51	08	17	43	53	31	09	60	34	34	61	93	66	01	94	37	13	24	09	75	29	21
55	42	48	76	50	13	89	69	00	05	99	45	82	01	53	86	68	81	36	50	75	20	17	94	47
80	50	67	83	01	97	76	21	64	34	62	43	02	84	38	13	60	26	32	36	81	43	17	56	41
03	64	65	44	02	75	41	33	91	28	82	97	57	38	49	27	26	97	34	44	26	12	00	68	24
14	53	75	37	91	43	95	15	13	26	33	27	45	48	33	80	80	26	69	76	04	87	83	58	32
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39	38	79	42	17	77	99	55	32	85	13	35	48	49	80	83	59	06	34	94	06	03	61	85	02
74	96	24	94	89	54	66	29	35	88	50	46	65	50	26	62	45	80	61	95	07	99	57	10	54
21	16	54	55	77	46	38	33	88	55	21	56	18	93	32	94	24	80	97	03	78	39	73	87	70
58	51	99	53	96	73	60	77	21	06	76	59	78	55	96	99	07	53	91	95	99	60	56	61	79
46	98	27	95	19	22	29	41	56	76	83	48	49	82	79	79	20	00	26	40	22	50	14	30	73
58	46	36	76	19	18	00	60	50	28	32	44	18	35	99	28	91	50	53	62	21	61	26	46	81
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93	54	23	72	70	09	36	16	24	04	74	05	65	29	64	67	37	28	13	98	01	48	29	75	89
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64	80	80	16	92	46	42	46	47	22	87	16	20	65	82	01	45	21	49	80	17	39	70	74	03
78	70	39	30	06	59	65	14	84	04	82	28	46	64	05	89	81	80	09	89	56	11	27	81	44
14	88	67	03	59	32	15	83	04	01	20	82	92	25	34	88	84	80	76	69	25	10	04	86	02
69	28	06	18	56	78	97	49	14	85	01	58	31	16	20	53	74	03	27	05	80	39	15	67	49
99	68	09	96	36	54	10	77	95	88	90	84	52	16	52	58	87	51	31	71	68	53	11	85	50
01	66	22	15	54	63	83	64	15	30	21	86	48	17	11	68	92	16	17	49	36	05	17	80	24
67	85	26	91	23	14	28	01	76	47	65	12	58	24	27	61	59	43	20	15	93	47	30	56	27
13	91	16	76	91	97	85	48	99	50	40	96	30	66	97	82	66	06	90	97	65	28	44	98	08
95	82	20	95	52	65	95	03	48	75	64	25	04	13	85	80	13	37	08	18	09	28	63	07	69
44	06	82	49	28	27	34	53	42	35	44	12	40	64	35	06	28	14	37	23	97	38	07	60	80
99	22	26	64	15	71	06	96	22	93	77	46	73	57	51	22	54	82	37	99	96	27	25	87	77
08	44	26	12	87	72	42	13	57	77	61	07	94	24	62	17	76	19	45	18	98	11	47	40	31
14	96	76	06	37	32	09	72	81	22	87	70	81	93	78	93	37	22	32	25	38	45	38	03	31
27	86	41	53	58	16	49	99	19	03	62	98	79	81	98	15	03	62	32	93	68	24	14	44	50
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89	14	37	94	03	22	32	45	42	61	97	83	04	26	30	48	49	40	99	99	69	96	13	94	21
34	13	53	15	32	42	02	58	32	14	83	73	02	82	49	25	62	91	14	94	70	72	64	50	51
72	11	79	75	79	36	07	12	92	61	89	93	77	82	08	23	74	75	67	56	37	45	35	13	44
19	72	57	61	99	08	62	02	26	82	52	90	72	51	94	84	59	79	34	19	95	76	21	49	91
96	99	76	63	90	27	60	94	15	70	17	74	92	31	85	24	47	55	64	51	91	47	13	39	69
44	15	86	76	18	15	57	29	51	62	95	84	20	83	01	11	90	66	80	81	40	43	65	87	35
33	83	94	07	50	18	89	86	16	50	09	97	04	76	51	41	20	56	50	20	33	53	70	10	22
53	07	06	16	30	84	43	40	57	32	18	09	47	16	69	41	03	38	24	02	16	41	58	39	58